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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

3102. **Proceedings of the International Symposium on Microchemistry.** Birmingham University, England. August, 1958. The following papers appear, in English, in this volume of the Proceedings of the Symposium, organised by the Midlands Section and the Microchemistry Group of the Society for Analytical Chemistry. **The use of pyrolytic and pyrohydrolytic cleavages in spot-test analysis,** F. Feigl, 3–5. **Specific and selective organic reagents,** F. J. Welcher, 6–21. **Practical applications of chemical microscopy,** P. W. West, 22–29. **Recent developments in the use of the ring oven,** H. Weisz, 30–35. **Role of perchloric acid in macro wet-oxidation of organic matter in the preparation for micro-determination of trace elements,** H. Diehl and G. F. Smith, 36–47. **Trace-element losses during mineralisation of organic material—a radiochemical investigation,** J. Pijck, J. Hoste and J. Gillis, 48–58. **Reliability of microchemical weighing,** G. F. 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3103. **Second Conference—Analytical Chemistry in Nuclear Reactor Technology. Part 2. Instrumentation, Remote-Control Techniques and Nucleonics.**

Sept. 29 to Oct. 1, 1958. Gatlinburg, Tenn. *U.S. Atomic Energy Comm.*, Rep. TID-7568 (Part 2), 1959, 242 pp.—The following papers are included in the report. **Instrumentation for chemical analyses. A. Applications of semi-conductor devices to potentiometric and coulometric titrations,** H. C. Jones. **B. Applications of operational amplifiers to controlled-potential and derivative polarography,** D. J. Fisher. **C. Applications of radio-frequency to reactor analysis,** R. W. Stelzner (Oak Ridge Nat. Lab., Tenn.), pp. 3–12. **Automatic analysing monitor,** H. G. Rieck, C. A. Ratcliffe and L. C. Schwendiman (General Electric Co. Hanford Atomic Products Operation, Richland, Wash.), pp. 13–23. **Operating experiences with oxide monitors for sodium systems,** E. F. Batutis (MSA Res. Corp., Callery, Pa.), pp. 24–32. **Instrumentation for X-ray diffraction studies of highly radioactive samples,** V. G. Scotti, J. I. Mueller and J. J. Little (Pratt and Whitney Aircraft Hot Cell Facility, Livermore, Calif.), pp. 33–41. **Fluorescence X-ray analysis of highly radioactive samples,** J. I. Mueller, V. G. Scotti and J. J. Little, pp. 42–51. **Remote analytical facility operational experiences,** G. A. Huff (Phillips Petroleum Co. Atomic Energy Div., Idaho Falls), pp. 55–64. **Remote pipetter for highly radioactive samples,** F. W. Dykes (Phillips Petroleum Co. Atomic Energy Div., Idaho Falls), pp. 65–75. **Analytical cave operations on fuel processing development samples,** R. P. Larsen, J. J. McCown and W. R. Sovereign (Argonne Nat. Lab., Lemont, Ill.), pp. 76–84. **Determination of hydrogen in irradiated reactor materials,** F. K. Heumann and L. A. Altamari (Knolls Atomic Power Lab., Schenectady, N.Y.), pp. 85–90. **Remotely controlled analytical facilities for the analysis of samples from the homogeneous reactor. Parts A to E,** C. Feldman, W. R. Musick, A. D. Horton, L. G. Farrar, B. B. Hobbs, W. D. Shults, M. T. Kelley, R. W. Stelzner, D. J. Fisher, U. Koskela, J. E. Attrill and J. L. Mottern (Oak Ridge Nat. Lab., Tenn.), pp. 91–141. **Special radiochemical analysis in the operation of Oak Ridge National Laboratory reactors,** G. W. Leddicotte and W. S. Lyon (Oak Ridge Nat. Lab., Tenn.), pp. 145–157. **Determination of uranium-235 by neutron activation using a radium - beryllium source,** W. W. Beyer, J. N. Lewis and G. L. Stukenbroeker (National Lead Co. of Ohio, Cincinnati), pp. 158–177. **Hot laboratory procedures used in burn-up analyses at Bettis Plant,** A. J. Moses (Westinghouse Electric Corp. Bettis Plant, Pittsburgh), pp. 178–183. **Estimation of boron in graphite by reactivity change,** J. J. Branson, G. E. Jessen, J. R. Clarke and W. W. Hawes (Naval Postgraduate School, Monterey, Calif.), pp. 184–191. **Radiochemical and mass-spectrometric studies of fission-product caesium,** A. J. Moses and H. D. Cook (Westinghouse Electric Corp. Bettis Plant, Pittsburgh), pp. 192–197. **Application of anion-exchange separations and gamma-spectrometry to radiochemical determinations of activated corrosion products,** D. Dutina and W. C. Judd (Knolls Atomic Power Lab., Schenectady, N.Y.), pp. 198–205. **Specific activity determination of cobalt-60 in neutron-activated corrosion products,** D. Dutina and W. C. Judd, pp. 206–213. **Determination of radioactive rare-earth elements in reactor effluent water,** L. J. Kirby, W. B. Silker and R. W. Perkins (General Electric Co. Hanford Atomic Products Operation, Richland, Wash.), pp. 214–229. **Radiochemical analyses for per-[pre]operational surveillance,** A. S. Goldin and C. P. Straub (Taft Sanitary Engng Center, Cincinnati), pp. 230–233. NUCL. SCI. ABSTR.

3104. **Analysis for industry.** A. M. G. Macdonald. *Ind. Chem.*, 1959, **35**, 556–558.—Analysis of organic materials by iodimetric and bromimetric methods is reviewed. Aldehydes, ascorbic acid, organic peroxides, phenols and sulphur-containing compounds are specially discussed, and the relationship between structure and reactivity is examined. (41 references.) S.C.I. ABSTR.

3105. **Current problems in chemical analysis. Automatic apparatus and procedures. Automation.** E. Lœuille. *Chim. Anal.*, 1959, **41** (11), 429–435.—A general discussion is presented of ways of effectively automatising apparatus and procedures in analytical separations and determinations so as to ensure increased precision and output and to facilitate rapid process control. Examples described to illustrate the degree of automation achieved include (in the laboratory) the completely automatic emission spectrometry of steel, the chromatographic determination of mixtures of amino acids, and (in the works) automatic spectrographic installations on Bessemer-converter floors and automatic gas chromatography with the Perkin - Elmer Vapour Fractometer in petroleum refineries. The resolution of the associated problems of sensitivity, rapidity and precision is also discussed. W. J. BAKER

3106. **Capillary analysis and paper chromatography.** A. Grüne (C. Schleicher & Schüll, Dassel, Kreis Einbeck). *Öst. ChemZtg*, 1959, **60** (11), 301–311.—An historical review is given, and some differences and similarities between capillary analysis and paper chromatography are discussed. B. B. BAUMINGER

3107. **Chelon approach to analysis. I. Survey of theory and application.** C. N. Reilley, R. W. Schmid and F. S. Sadek (Univ. N. Carolina, Chapel Hill, U.S.A.). *J. Chem. Educ.*, 1959, **36** (11), 553–564.—A review is presented of the use of chelons (a generic term for compounds that form stable, soluble complexes with metal ions and may be used as titrants for metal ions). (39 references.)

3108. **Zone melting, with some comments on its analytical potentialities. A review.** E. F. G. Herington (Pure Compounds Group, Nat. Chem. Lab., Teddington, Middx., England). *Analyst*, 1959, **84**, 680–689.—Zone refining and zone levelling are treated theoretically and practically. Among the practical considerations are the measurement of the effective distribution coeff., k (*i.e.*, the ratio of the concn. of the impurity in the solid to its concn. in the liquid from which the solid has just separated) and the effects of speed of zone movement, volume change and zone length. Some experimental techniques are described and examples are given of some unusual separations. (46 references.) A. O. JONES

3109. **The evolution of certified reference materials.** J. L. Hoffman (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1934–1940.—The development of standard reference materials in the U.S.A. (by the National Bureau of Standards) and in Great Britain is reviewed historically. The dependence of these materials on progressive development in analytical methods and, in turn, their important influence on the development of new methods are discussed, with special reference to spectrographic standards for

quant. work and the new procedures for the separation of Nb and Ta in the presence of Ti. (12 references.) W. J. BAKER

3110. **Use of tri-*n*-octylphosphine oxide in analytical chemistry.** J. C. White. ASTM Symposium: Solvent extraction in the analysis of metals, 1958. 1959, 27–35.—Data obtained in studies of this solvent as a reagent in the separation of metal ions by liquid - liquid extraction are summarised. Hexavalent chromium is readily extracted from acid soln., but Cr^{III} has so far been unextractable, and the reagent thus provides a means of separating these two states. Experiences with Zr, Mo^{VI}, U^{VI}, Bi^{III}, Th, Nb^{V}, Ta and Ti are included. Formation of coloured species, selectivity and soln. stripping are considered.

METALLURG. ABSTR.

3111. **PAM. (Picolinaldoxime methiodide.)** M. Halse and O. Skogan (Norsk Medisinaldepot, Oslo, Norway). *Medd. Norsk Farm. Selsk.*, 1959, **21** (11), 141–157.—A review, with observations on methods of synthesis and determination, stability in aq. soln., and the detection and determination of products of hydrolysis. (16 references.)

P. S. ARUP

3112. **Flavylium perchlorate as a reagent in paper chromatography.** K. Formanek and H. Höller (Inst. Path., Univ. Wien, Austria). *J. Chromatography*, 1959, **2** (6), 652–654 (in German).—Flavylium perchlorate (a 25% soln. in acetic acid) reacts on paper with a number of substances giving colours that are easily seen in visible and u.v. light. A table of 22 reactants, some of them giving highly specific colours, is given. These include adrenaline, pyrogallol, 4-aminosalicylic acid and indolylacetic acid. G. S. ROBERTS

3113. **Analytical chemistry by means of organic compounds. XXV. 1-Hydroxyacridine as a new reagent (neo-oxine). (1).** Masayoshi Ishibashi, Yuroku Yamamoto and Hirohiko Yamada (Chem. Dept., Fac. Sci., Kyoto Univ., Sakyo-ku). *Bull. Chem. Soc. Japan*, 1959, **32** (10), 1064–1068 (in English).—The absorption spectra of 1-hydroxyacridine were obtained both in aq. and $CHCl_3$ soln., and the pK_a and pK_b values were determined. The pK_a value is slightly greater than that of oxine, and it is suggested that the stability of a metal chelate with 1-hydroxyacridine will have values of the same or of a higher order than those of the oxine chelate, because there is a direct relation between the basicity of a chelating agent, as measured by pK_a values, and the stability of the chelates it forms, as cited by Morrison and Friser ("Solvent Extraction in Analytical Chemistry," John Wiley & Sons, Inc., New York, 1957). The various aspects of solvent extraction with $CHCl_3$ are investigated. The optimum pH range for extraction for each element is determined and it is found that the range is narrow compared with that of the oxine chelate. The percentage extracted is determined and it is found that Cu, Ni, Co and Zn are almost completely extracted under the conditions investigated. I. JONES

3114. **Qualitative analysis of cations by the use of metal indicators. II. Investigations with 1-(2-pyridylazo)-2-naphthol (PAN).** W. Berger and H. Elvers (Entwicklungslab. der Valvo G.m.b.H. Radioröhrenfabrik, Hamburg). *Z. anal. Chem.*, 1959, **171** (3), 185–193 (in German).—Several metals form complexes with PAN in aq. soln., many of which are sol. in $CHCl_3$; this is the basis of the qual. scheme described. *Procedure for complexes formed at pH* 10—Buffer the sample soln. with NH_4Cl - aq. NH_3 and treat with a 0·1% soln. of PAN in ethanol, then extract the complexes of Ni, Co, Cu, Zn, Cd, Mn and UO_2^{2+} with $CHCl_3$. Copper is detected by shaking with 0·01 *M* EDTA (disodium salt) (the $CHCl_3$ layer turns yellow), Cd with 0·01 *M* Na diethyldithiocarbamate (**I**), Mn with acetate buffer (pH 6), and Zn with 0·02 *N* H_2SO_4. *Complexes formed at pH* 6—Add acetate buffer to the sample soln. and treat with PAN; the complexes of Ni, Co, Cu, Zn, Fe, UO_2^{2+}, In and Pd are sol. in $CHCl_3$. Shaking with 0·05 *M* KCN gives a colour reaction with Cu and Pd, EDTA reacts with In, and H_2SO_4 with Zn. When UO_2^{2+} are present, Na acetate buffer cannot be used. *Complexes formed at pH* 3—Adjust 10 ml of sample soln. to pH 3 with acetic acid, add 1 ml of 1% NaF soln. and treat with PAN. Complexes of Cu, Co and Pd are sol. in $CHCl_3$; Cu is detected by shaking with EDTA and Pd with **I**. Certain specific reactions are also described.

P. D. PARR-RICHARD

3115. **New method for the separation of elements of group 1 by paper chromatography.** M. B. Čelap and Z. Radivojević (Fac. of Sci., Inst. of Chem., Belgrade, Yugoslavia). *Bull. Soc. Chim. Belgrade*, 1958–1959, **23–24** (1–2), 59–66.—An effective separation of Ag^+, Tl^+, Pb^{2+} and Hg^{2+} ($\simeq$ 0·1 *M*) can be achieved in $\simeq$ 3 hr. at 20° $\pm$ 1° by ascending paper chromatography (Whatman No. 1, 25 cm × 3 cm) with the solvent mixture methanol (60 ml) - 11 *N* HNO_3 (40 ml). The R_F values are Ag^+ 0·29, Tl^+ 0·39, Pb^{2+} 0·51, and Hg^{2+} 0·75. The spots are detected by dipping the chromatogram in a soln. of ammonium sulphide; the lower limit of detection is 1×10^{-5} g. The normality of the HNO_3 can be varied from 6 to 12, but 11 *N* is optimum. The sample soln. should be prepared by reduction (with metallic zinc) of the pptd. chlorides of the group-1 metals, followed by dissolution of the metals formed in 8 *N* HNO_3. (From English summary.)

W. J. BAKER

3116. **Chemical indicators. V. The chelatometric indicator Eriochrome cyanine R, its acid - base properties and formation of metal complexes.** V. Suk and V. Miketuková (Dept. of Anal. Chem., Charles' Univ., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3629–3636 (in German).—In an acid medium, Eriochrome cyanine R (C.I. Mordant Blue 3) (**I**) forms an orange dipolar ion. With increasing pH, the colour changes to red, then yellow, then violet in strongly alkaline medium (pH >10). This bathochromic effect is combined with a hyperchromic one. The dissociation constants of **I** were calculated by means of spectrophotometric measurement. The chelating power of **I** permits colour reactions with many cations. The formation of these depends on the H^+ concn.; in an acid medium complexes with ter- and quadrivalent cations are formed, while those with bivalent cations are formed in alkaline soln. J. ZÝKA

3117. **"Three-phase titration" as a new analytical aid.** H. Lux, T. Niedermaier and K. Petz (Anorg.-chem. Lab., Tech. Hochschule, Munich). *Z. anal. Chem.*, 1959, **171** (3), 173–176 (in German).—When a soln. of Ag^+ containing large amounts of alkali-metal salts is titrated with a soln. of *p*-dimethylaminobenzylidenerhodanine (**I**) in CCl_4, the ppt.

formed from Ag^+ and **I** collects at the phase boundary and the end-point is indicated by the colour of the unchanged reagent in the CCl_4 layer. Other derivatives of rhodanine were tested as reagents for Ag^+; N-methylanilino-5-rhodanylpentamethine was particularly satisfactory. *Reagent*—Add excess of **I** to 100 ml of CCl_4, warm at 50° and filter after standing overnight. Dilute with 100 ml of CCl_4 and titrate against standard Ag^+ soln.; store under 0·1% H_2SO_4. *Procedure*—Titrate 5 ml of soln. (pH 2 to 5), containing 3 to 15 μg of Ag^+, with reagent, shaking for 2 to 3 min. between each addition, until a yellow colour persists in the CCl_4 layer. The ppt. should be red or violet; 1 mole of **I** reacts with 1 mole of Ag^+. The relative error is ±0·4% for 14 μg of Ag^+ per 5 ml (4 determinations). P. D. PARR-RICHARD

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

3118. **Some recent developments and current problems in metal analysis.** R. M. Fowler (Union Carbide Metals Co., Niagara Falls, N.Y., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1949–1951.—The progress made in the chemical analysis of metals during the past 40 years is illustrated by reference to the determination of carbon in steel and, during the past 15 years, to the use of the direct-reading spectrograph, the X-ray spectrometer and the mass spectrometer. (7 references.) W. J. BAKER

3119. **Recent developments and current problems in inorganic analytical chemistry. Nuclear materials.** C. J. Rodden (U.S. Atomic Energy Comm., New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1940–1945.—The following subjects are discussed—(*i*) the chemical analysis of uranium, thorium, plutonium and beryllium and their alloys with other metals, (*ii*) the determination of the isotopic composition of uranium, and (*iii*) the determination of minor impurities in nuclear fuels and moderators, namely, (*a*) those elements that are undesirable because of nuclear absorption, and (*b*) those that unfavourably affect the metallurgical processing. (39 references.) W. J. BAKER

3120. **Omega Chrome black blue G as a colorimetric reagent for the micro-determination of various cations.** A. A. A. El Raheem, A. Aziz Amin and F. A. Osman (Public Health Lab. and Nat. Res. Centre, Cairo, Egypt). *Z. anal. Chem.*, 1959, **171** (6), 420–432 (in English).—Omega Chrome black blue G (C.I. Mordant Black 38) is suitable for the determination of microgram quantities of Co in the presence of Cd^{2+}, Sr^{2+}, Fe^{2+}, Fe^{3+}, Ca^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+} and, in particular, Ni^{2+}; Cu^{2+}, Cd^{2+}, Pb^{2+} and Mg^{2+} may also be determined by a similar procedure. The soln. is buffered to pH 10 in a 25-ml flask, 1 ml of aq. dye soln. (0·1%) and 5 ml of 0·01 *M* EDTA (disodium salt) are added and the mixture is diluted to the mark with water; the extinction is measured at 625 mμ. A reagent blank is deducted and the result is referred to a calibration graph. Manganese was found to interfere owing to the reducing action of ascorbic acid, used to prevent pptn. of Mn at the pH used, on the Co - dye complex. The dye may also be used to detect Co in the presence of the metals named. H. M.

3121. **Use of metal reductors and amalgams in chemical analysis. I. Silver reductor.** J. Doležal, J. Drahonovský and J. Zýka (Dept. of Anal Chem., Charles' Univ., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3649–3653 (in German).—Conditions have been established for the quant. reduction of MnO_4^-, $Cr_2O_7^{2-}$, BrO_3^-, Sb^{5+}, Ce^{4+} and Ir^{4+}. In 5 to 6 *N* HCl, Sb^{5+} can be reduced to Sb^{3+} in the presence of an excess of As^{3+} and Sn^{4+}. *Procedure for Sb*—Mix the sample (2 g for 0·5 to 2% of Sb, 1 g for 2 to 5%, or 0·5 g for 5 to 10%) with six times its wt. of a mixture of sulphur and anhyd. Na_2CO_3 (3:1), cover with 2 g of the mixture and fuse. Treat the melt with hot water (100 ml) and set aside on the water bath. If the soln. is green, add KCl (2 g) and heat again. Decant off the supernatant liquid, and wash the residue by decantation with 1% Na_2S soln. and then with a little hot 0·5% KCl soln. Acidify the combined liquids with acetic acid, and allow the pptd. sulphides to settle. Decant the supernatant liquid through a filter, and wash the residue with a little hot water. Dissolve the residue in 0·2 *N* NaOH (25 ml), heat, and filter through the same filter. Wash the sulphur on the filter with hot water, and treat the combined filtrates with conc. H_2O_2 soln. (5 ml). Remove the excess of H_2O_2 by boiling, evaporate the liquid to 20 ml, add conc. HCl (30 ml), heat to 65° to 75° and pass it through a silver reductor. Titrate the Sb^{3+} with 0·1 *N* $KBrO_3$, potentiometrically, or visually with methyl orange as indicator. Similar procedures are described for the determination of Fe and V in ferrovanadium with $Ce(SO_4)_2$ soln., and of Cu and Fe in brass with $K_2Cr_2O_7$ soln. J. ZÝKA

3122. **Amperometric determination of metals forming normal selenites.** G. S. Deshmukh, M. G. Bapat, E. Balkrishnan and M. C. Eshwar (Chem. Lab. Benares Hindu Univ., India). *Z. anal. Chem.*, 1959, **170** (2), 381–383 (in English).—Silver, Pb and Hg can be determined by pptn. as the selenites from neutral soln. with an excess of standard H_2SeO_3 soln., followed, after filtration, by the amperometric titration of the excess of H_2SeO_3 with standard NaOBr soln. (*cf. Anal. Abstr.*, 1959, **6**, 139). The procedure is rapid and has a precision of ≃ 1% for 10 to 100 mg of Ag, Pb or Hg. W. T. CARTER

3123. **Emission-spectrometric determination of the gaseous elements in metals.** V. A. Fassel, W. A. Gordon, R. J. Jasinski and F. Monte Evens. *Rev. Univ. Mines*, 1959, **15** (5), 278–281 (in English).—The dissolved gases in metals are liberated by the use of a d.c. arc in an atmosphere of pure Ar, and comparison of the lines of O, H and N with the lines of Ar in the visible region of the spectrum is used for determination of the gas contents. A sample (1 g) of Fe, Ni, V or Cu is supported on a specially turned graphite electrode so that the rim of the cup-shaped electrode dissolves in the molten sample; O and N were determined in the range 0·002 to 0·2% in this way. For Zr, Ti, Nb and Th a different electrode-shape is needed, and 100 to 300 mg of the metal is placed in a dished platinum disc weighing 500 mg; the metal sample is alloyed with the platinum by passing a current of 15 amp.; the current is then increased to 30 amp. to liberate the dissolved gases; as before, the intensities of certain lines of H and O are compared with lines of Ar. Details are given of the technique for supporting the sample, for purifying the gases, and

for changing the samples in a discharge chamber which is partially evacuated.

METALLURG. ABSTR.

3124. **Spectrographic analysis of inorganic non-metallic materials by the barium chloride flux method.** U.K.A.E.A. (Chem. Div., A.E.R.E., Harwell). AERE-AM 57, 1959. 13 pp.—The method has been written in its present form by J. C. Cotterill; it is based upon a technique suggested by Fitz and Murray (*Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 145) and on Report No. CI/R-29 (Chemical Inspectorate, Ministry of Supply) by Mastyn, Jury and Parker.

3125. **Quantitative γ-ray spectrometric analysis of nuclide mixtures: consecutive standard sources nullification.** D. G. Olson (Phillips Petroleum Co., Atomic Energy Div., Idaho Falls, Idaho). *U.S. Atomic Energy Comm.*, Rep. IDO-14495, Oct., 1959. 41 pp.—Conventional methods for analysing fission-product mixtures are lengthy and difficult. γ-Scintillation spectrometry shortens the analysis time and gives a visible picture of what is being counted. However, for complex spectra, the graphical representation and interpretation of data require tedious plotting and data reduction time. In the proposed method a sample of mixed fission products is scanned by a 256-channel γ-spectrometer. Instrumental analysis of this spectrum is made, by using complement, nuclide subtraction technique. Specific activities are determined for each nuclide by using standard sources. The time required to make an analysis when four isotopes are present would be ≃ 30 min. Statistical evaluation of the method has been made for ^{144}Ce, ^{106}Ru, ^{137}Cs and ^{95}Nb in the experimental work. Since standard sources are required for the analysis this method is limited to fission products with reasonably long half-lives. NUCL. SCI. ABSTR.

3126. **Amperometric titration of copper, palladium and cobalt by means of 1-nitroso-2-naphthol with a rotating tantalum electrode.** V. A. Zhadeev and L. A. Glazunov. *Uzbek. Khim. Zhur.*, 1959, (3), 24–33; *Ref. Zhur., Khim.*, 1960, (3), Abstr. No. 8827.—The rotating platinum electrode is compared wth the tantalum electrode. It is shown that 1-nitroso-2-naphthol (**I**) is reduced and oxidised with the formation of two waves; $E_{\frac{1}{2}}$ *vs.* the S.C.E. are −0·15 V and +0·6 V in an acetate buffer medium and −0·45 V and +0·4 V in a soln. 0·2 *M* with respect to NH_3 (NH_4Cl - aq. NH_3) (2:1). The heights of the cathode and anode waves are proportional to the **I** concn., the cathode wave being four times as high as the anode wave. With a tantalum electrode the limiting currents of oxidation and reduction of **I** are much more stable than with a platinum electrode. Amperometric titrations with **I** of Cu (> 0·2 mg in 40 ml of soln.) and of Pd are described; a basal soln. of 0·2 *M* acetate buffer soln. (Na acetate - acetic acid) (2:1) is used with a +0·9-V oxidising current and a −0·3-V reducing current. An anode current is used for the titration of small amounts of Cu and Pd and also if easily reducible impurities are present. Citrate, tartrate, NO_3^-, SO_4^{2-}, Cl^- and F^-, 100 to 50-fold amounts of Mg, Ca, Sr, Ba, Al, Zn, Cd and Sb, 10-fold amounts of Sn and Bi and equal amounts of Ni, Cr, Hg and Fe^{3+} do not interfere with the determination; Fe^{3+} are easily masked by means of F^-. In the presence of Mn a cathode current is used for the titration. Copper can be determined in brass and Duralumin. The titration of Co with **I** in either ammoniacal or acetate medium is not satisfactory. K. R. C.

3127. **Anodic amalgam voltammetry. I. Principle of the method. II. Determination of small amounts of lead, cadmium, bismuth and thallium.** R. Neeb (Inst. f. anorg. und anal. Chem., Univ. Mainz, Germany). *Z. anal. Chem.*, 1959, **171** (5), 321–339 (in German).—After the electrolytic separation of metals at amalgamated platinum electrodes and rapid re-solution of the amalgams by reversing the current, reproducible results can be obtained for trace amounts of metals (0·1 μg) under controlled conditions by measuring the peak heights on the current - voltage curve. Detailed procedures for the determination of traces of Pb, Cd, Bi and Tl are given. B. B. BAUMINGER

3128. **Electrode polarisation during polarographic determination of antimony, bismuth, lead and tin.** N. A. Lektorskaya and P. N. Kovalenko. *Uch. Zap. Rostov. na Don Univ.*, 1958, **41**, 95–105; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,286.—Data concerning electrode polarisation during the reduction of Bi, Sb, Pb and Sn in soln. of zinc salts in the presence of HCl and NaF are given. Concentration polarisation during the reduction of Bi and Pb with soln. of zinc salts in the presence of HCl and NaF, and a considerable chemical polarisation during the electrolysis of Sn in the presence of NaF ($2{\cdot}38 \times 10^{-3}$ *M*), have been confirmed. Increase of the concn. of NaF up to $4{\cdot}76 \times 10^{-3}$ *M* causes a rapid drop in the Sn diffusion current and the polarographic wave becomes deformed. Chemical polarisation during the reduction of Sb with zinc salts, with HCl and NaF as supporting electrolyte, has been studied and the dependence of the "polarographic" characteristics of Sb on the concn. of NaF has been shown. The dependence of height and shapes of the diffusion waves and half-wave potentials of Bi, Sn, Sb and Pb on the concn. of the supporting electrolytes has also been studied. Optimum concn. of NaF and the conditions for the joint polarographic determination of Bi and Sb as well as of Pb and Sn are given. W. ROUBO

3129. **Determination of tritium in a proportional counter. [I.]** W. G. Verly, G. Hunebelle and G. Thomas (Univ., Liège, Belgium). *Nukleonik*, 1959, **1**, 325–329 (in French).—A method for the determination of ^3H in hydrogen in a counter of the Bernstein - Ballentine type operating in the proportional zone is presented. The filling is completed with methane up to a pressure of 760 torr. The partial pressure of the tritiated hydrogen can attain 500 torr. With one tube, a voltage of 4500 V is used for the measurement on the condition that the hydrogen pressure does not exceed 50 torr and that the total pressure does not vary more than 10 torr from its optimum value of 760 torr. The background is 90 counts per min. No contamination of the counter tube by tritiated hydrogen is observed. The counting yield is quantitative for disintegrations produced in the cathode cylinder. The error for the complete measurement (introduction of the sample into the tube and counting) is 2%.

II. Preparation of samples. P. A. Ciccarone, G. Thomas and W. G. Verly. *Ibid.*, 1959, **1**, 329–332.—The tritiated organic compound is burned in a current of O, and the water of combustion is transferred, under vacuum, to a blank tube containing magnesium turnings. The tube is then sealed and heated to 550° for 1 hr. The ^3H in the hydrogen

from the reduction is measured in a proportional counter in the presence of methane. Neither the combustion apparatus nor the magnesium turnings is a source of H or other gases, so that the measurement of the specific activity of the reduction hydrogen can be used to calculate the concn. of ^3H in the organic compounds. The memory effect in the combustion apparatus is negligible and the error in the complete apparatus is $\simeq 1{\cdot}5\%$.

NUCL. SCI. ABSTR.

3130. **Determination of water by direct amperometric measurement.** F. A. Keidel (Engng Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2043–2048.—From 1 to > 1000 p.p.m. of H_2O in a gas, liquid or solid can be determined in an electrolytic cell (illustrated) wherein all entering H_2O is continuously and quant. absorbed (by P_2O_5 on the cell wall) and electrolysed at 25°. The measured current is proportional to the rate of entrance of H_2O into the cell, *e.g.*, at a gas flow of 100 ml per min. (preferred) the electrolysis current is $13{\cdot}2$ μA per p.p.m. (by vol.), which corresponds to $7{\cdot}4 \times 10^{-6}$ g of H_2O per min. A liquid sample is analysed by vaporisation or (and also for a solid sample) by stripping the H_2O with an inert gas. The accuracy is normally limited only by the precision of the electrical and flow-meter components. Hydrogen fluoride and NH_3 should be absent; control of other interferences, operating variables (*e.g.*, entrance of extraneous H_2O when determining low concn.), and practical applications are discussed. The method is specially suitable for the analysis of inert gases, of gas and liquid process-streams, and for determining the permeability of polymer films under steady-state and transient conditions.

W. J. BAKER

3131. **Single-stage enrichment factor in the separation of lithium isotopes by ion-exchange.** G. M. Panchenkov, E. M. Kuznetsova and O. N. Kaznadzei. *Atomnaya Energiya*, 1959, **7** (6), 556–557.—Cation-exchange resins, lithium salts and soln. concn. were studied. Cationites of the sulphonated coal type, and aluminium silicate, gave approx. the same separation coeff. ($^7Li/^6Li$). Soln. of lithium hydroxide, carbonate, benzoate and chloride, all at concn. of 0·1 *N*, gave separation coeff. of 1·009, 1·003, 1·003 and 0·996, respectively. Lithium hydroxide at concn. of 5 *N*, 0·5 *N*, 0·1 *N* and 0·005 *N* gave separation coeff. of 1·021, 1·015, 1·009 and 0·985, respectively.

A. BURWOOD-SMITH

3132. **Photometric determination of potassium with dipicrylamine (hexanitrodiphenylamine).** K. Riedler and L. Schreiner. *Chem. Tech., Berlin*, 1959, **11** (11), 593–596.—The determination of K (0·5 to 18 mg) with hexanitrodiphenylamine in a Pulfrich photometer with S42 filter is accurate to within ±2%. The optimum pH range is 7 to 8. Ammonium salts interfere only in large concn. but Rb and Cs behave similarly to K. *Procedure*—To the aq. soln. (5 ml) add 0·1 *N* Na hexanitrodiphenylamine (5 ml) satd. with K hexanitrodiphenylamine. Set aside for 2 hr. at 0° and collect the ppt. on a G4 filter. Wash with ice-cold satd. K hexanitrodiphenylamine soln. (3 × 5 ml) and then with ice-cold water (5 ml). Dissolve the ppt. in acetone (20 ml) and dilute with water to 250 ml; dilute a 5-ml aliquot with water to 250 ml and determine the extinction. Read the content of K from a calibration curve.

J. P. STERN

3133. **Determination of caesium-137.** U.K.A.E.A. (Chem. Div., A.E.R.E., Harwell). AERE-AM 2, 1959, 8 pp.—The method is based on that of L. E. Glendenin and C. M. Nelson (National Nuclear Energy Series, Vol. IV, 9, Paper 283); it was written in its present form by G. J. Hunter.

3134. **Redox indicators in trace analysis. Colorimetric determination of copper(II) with Variamine blue.** Z. Gregorowicz (Inst. Inorg. Chem., Tech. High School, Gliwice, Poland). *Z. anal. Chem.*, 1959, **171** (4), 246–250 (in German).—Variamine blue (**I**) can be used as a redox indicator in the pH range of 2 to 6; the working temp. should be ≯ 30°. The effects of reagent concn., reaction time and pH on the reaction of **I** with Cu^{II} are discussed; Beer's law is followed for concn. of 10 to 100 μg of Cu per 50 ml. *Procedure*—Add sufficient buffer to the test soln. to give a pH of 4 to 6, add 1 ml of a 1% soln. of **I** and dilute to 50 ml. After 15 min. measure the extinction in a Pulfrich photometer, with filter S57. As little as 0·0001% of Cu in zinc, cadmium or ammonium salts can be determined. *Preparation of reagent*—Grind 0·2 g of **I** with H_2O (20 ml), add 1 *N* NaOH (5 ml) and shake with benzene (20 ml). Extract the benzene layer with 20% acetic acid (20 ml) and allow the extract to stand for 3 to 4 hr. before use.

P. D. PARR-RICHARD

3135. **Rapid extraction of copper(II) with 2-thenoyltrifluoroacetone. Direct colorimetric determination in the organic phase.** Shripad M. Khopkar and Anil K. De (Dept. of Chem., Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1959, **171** (4), 241–246 (in English).—The reaction of 2-thenoyltrifluoroacetone (**I**) with Cu^{II} has been studied; extraction of the complex with benzene is complete in the pH range from 2·4 to 6. *Procedure*—To a soln. containing 0·4 to 4·5 mg of Cu add 10 ml of buffer soln. (60 g of acetic acid and 14 g of ammonium acetate in H_2O, adjusted to pH 3·5 with aq. NH_3 and diluted to 1 litre) and shake for 10 min. with 10 ml of 0·15 *M* **I** in benzene. Wash the aq. layer with 5 ml of benzene, make the benzene layer and washings up to 25 ml and measure the extinction at 430 mμ *vs.* a reagent blank. Beer's law is followed for concn. of 16 to 180 μg of Cu per ml; the colour is stable. Extraction is enhanced in the presence of $(NH_4)_2SO_4$, Na_2SO_4 or $MgSO_4$; small amounts of Ag, Hg^{II}, Bi, citrate or tartrate are allowable, but Co, Ni, Fe^{III}, Al, Ce^{IV}, Th, U and Zr interfere. Phosphate, Mn^{II} and Cr^{III} interfere less seriously.

P. D. PARR-RICHARD

3136. **Titrimetric methods by means of redox-shift. I. Volumetric determination of copper with ferrous sulphate.** C. Mahr and B. Seeger (Chem. Inst., Univ. Marburg/Lahn). *Z. anal. Chem.*, 1959, **171** (5), 343–349 (in German).—Apparatus is described and illustrated for the potentiometric determination of Cu in an atmosphere of pure N (max. 0·01% of O). To the soln. (5 to 50 mg of Cu) are added 10 ml of acetate buffer soln. (*M*), 5 ml of aq. KF soln. (20%) and 10 ml of KI soln. (0·2 *M*) and the mixture is diluted to 50 ml. The soln. is heated to 60° in a stream of N and titrated with 0·1 *N* $FeSO_4$. The mean error is 0·25%. The polarovoltric titration method of Walisch and Ashworth (*Anal. Abstr.*, 1959, **6**, 925) has been studied, but the end-point cannot be calculated from the polarisation voltage changes before and after the largest deflection. In the visual end-point detection, the use of two indicators, *i.e.*, Variamine blue (C.I. Azoic Diazo Component 35),

a redox indicator, and 3-methylbenzothiazoline-2-azino-5-(5:8-dihydro-8-hydroxyquinoline), a selective dye for Cu, is described. The colour change in the former is from pink to colourless, and in the latter from light blue to pink; NH_4^+, Ca, Ba, Zn, Cd, Pb, Ti, Zr, Sb^V, Mo^{VI}, Mn, Co and Ni do not interfere, but the titration fails in the presence of Al, Br, Fe^{3+}, Hg, Bi, As, Sb^{III}, Au, V^V and U^{VI}. The method is applicable to brass and bronze samples. B. B. BAUMINGER

3137. **Amperometric determination of copper with mandelamidoxime.** B. Banerjea and B. Chakravarty (Dept. of Inorg. and Anal. Chem., Indian Ass. for Cultiv. of Sci., Calcutta). *Z. anal. Chem.*, 1959, **171** (1), 4–9 (in English).—By the method described 0·5 to 8·0 mg of Cu^{II} can be titrated with an aq. soln. of mandelamidoxime (**I**) at an applied potential of −0·5 V *vs.* the S.C.E. in an NH_4Cl - aq. NH_3 buffer soln. (**II**) of pH 8·3 to 8·8, containing gelatin soln. as a max. suppressor. The copper soln. is neutralised to ≃ pH 6 with dil. NaOH soln., **II** is added, followed by the requisite quantity of gelatin soln. (0·5%), and the mixture is diluted to a known volume. An aliquot is transferred to the titration cell and titrated with **I** of suitable concn. (≃ 5 to 10 times the *M* concn. of Cu in the soln.). Serious interference is caused by all commonly associated elements (with the exception of Cd) and preliminary separation is then necessary. The error is < 1%. B. B. BAUMINGER

3138. **Analytical uses of 8-mercaptoquinoline (thio-oxine) and its derivatives. XV. Specific copper flotation reaction with 6-chloro-8-mercaptoquinoline disulphide.** Yu. A. Bankovskiĭ and E. F. Lobanova. *Izv. Akad. Nauk Latv. SSR*, 1959, (7), 85–90; *Ref. Zhur., Khim.*, 1960, (3), Abstr. No. 8835.—A qual. copper flotation reaction is based on the specific reduction of 6-chloro-8-mercaptoquinoline disulphide by Cu^+ to give $Cu(C_9H_5NClS).(C_9H_6NClS)$, which is insol. in H_2O and practically all organic solvents (except bromoform) but can be formed as a brown ppt. at the interface with the solvent phase. This reaction can be used to detect microgram amounts of Cu in a soln. containing very large amounts of many foreign elements. Cations that are reducible with ascorbic acid interfere if ascorbic acid is used for the reduction of Cu^{2+} to Cu^+; cations (*e.g.*, Au, Ag, Hg and Se) that form insol. salts and co-precipitate with Cu also interfere. Platinum metals and Se are retained in soln. in an ammoniacal medium. Large amounts of the common anions (except CN^-, oxalate, $S_2O_3^{2-}$ and $S_2O_4^{2-}$) do not interfere. The reaction can also be used for the gravimetric determination of Cu and for the separation of large and small (microgram) amounts of Cu from large amounts of Fe, Ni, Co, Al, Mn, Zr, Ge, Sb, Bi, V, In, Ga, Th, and other metals. K. R. C.

3139. **Polarographic determination of small amounts of lead and cadmium in copper electrolytes (rapid method).** P. N. Kovalenko. *Uch. Zap. Rostov. na Don Univ.*, 1958, **41**, 123–134; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,350.—A combined electrochemical method for the determination of small amounts of Cd and Pb in the presence of large amounts of Cu has been developed. Copper and Pb are separated simultaneously from Cd by the electrolysis of 1·2 to 1·4 *N* HNO_3 soln. at 1·95 V and 50°. Lead is deposited as PbO_2 at the anode (quantitatively in 50 min.), and is determined by weighing the washed and dried anode. For the quantitative deposition of Cu at the cathode the electrolysis should be carried out for ≮ 100 min. Cadmium is determined polarographically with Na citrate, aq. NH_3 and NH_4Cl (3 g of Na citrate, 10 g of NH_4Cl and 26 ml of 25% aq. NH_3 in 200 ml of water) as basal soln. A complete analysis for Pb, Cu and Cd takes 2 to 3 hr. W. ROUBO

3140. **Separation of silver from lead by extraction of tributylammonium thiocyanatosilver.** M. Ziegler, H. Sbrzesny and O. Glemser (Anorg.-Chem. Inst. der Univ. Göttingen). *Z. anal. Chem.*, 1959, **171** (4), 250–254 (in German).—When tributylammonium acetate (**I**) and KSCN are added to a soln. of Pb or Bi at pH 5, no pptn. occurs, and small amounts of the silver complex can be extracted with dichloromethane (**II**). Copper must first be removed from the weakly acid test soln. by adding cupferron and extracting with **II**. *Procedure*—Adjust the pH of the soln. to 4·9 with 10 ml of buffer soln. (200 g of Na acetate and 20 ml of acetic acid in H_2O to make 1 litre). Add 8 ml of **I** and 4 ml of 40% KSCN soln., then shake with 10 ml of **II** and remove the organic phase. Add 4 ml of **I** and 2 ml of KSCN soln. and re-extract twice with **II**. After washing the combined organic phases with H_2O (20 ml), add 5 ml of acetone - conc. HCl (100:1) and 10 ml of CS_2. Pass H_2S for 5 to 7 min., filter, and wash the ppt. with CS_2 (3 × 5 ml), dry at 130° for 30 min. and weigh. *Preparation of reagent*—Mix 100 ml of tri-*n*-butylamine and 100 ml of H_2O with activated charcoal (15 g), add 50 ml of acetic acid, stir and cool. Add H_2O (100 ml) and acetic acid (50 ml), stir for 15 min. and filter. Add H_2O (70 ml), acetic acid (70 ml) and charcoal (15 g) to the filtrate, stir for 30 min. and filter. P. D. PARR-RICHARD

3141. **Polarographic determination of gold on a rotating platinum micro-disc electrode.** M. B. Bardin and V. S. Temyanko (Kishinevsk State Univ.). *Zhur. Anal. Khim.*, 1959, **14** (6), 677–681.—It is shown that $HAuCl_4$ is reduced to metal on the rotating platinum micro-disc electrode at + 0·6 V. Dissolved O does not interfere. Clear reduction waves are obtained in basal soln. of KCl, NaCl, LiCl, NH_4Cl, $NaNO_3$, $NaClO_4$, HCl, H_2SO_4, HNO_3 and $HClO_4$; in 0·1 *M* Na acetate the height of the wave is slightly reduced, and in a soln. of ethylamine hydrochloride the slope of the rising portion of the curve is increased. The wave height is directly proportional to the concn. of Au in the range 2×10^{-4} to 3×10^{-6} *M*, with an average error of ≃ ± 3%. C. D. KOPKIN

3142. **Determination of beryllium oxide in copper - beryllium alloy.** Chzhou-Sin, F. Sh. Muratov and A. V. Novoselova (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1959, **25** (11), 1292–1293.—The sample (1 g), together with 10 ml of methanol, is treated gradually, under a reflux condenser, with 50 ml of methanol containing 6 ml of liquid Br. The soln. is mixed with 50 ml of an 8% soln. of conc. HCl in methanol and the insoluble matter is collected after 30 min. and washed with methanol. It is then dissolved in a mixture of 10 ml of conc. H_2SO_4 and 10 ml of conc. HNO_3, the soln. is evaporated nearly to dryness, the residue is dissolved in water, the soln. is diluted to 100 ml and the acid content of the soln. is determined by titration. An aliquot (10 ml) is neutralised and treated further with NaOH soln. (20 ml of 0·25 *N*), then 3 ml of a

0·02% soln. of beryllon II (*cf.* Mašek, *Anal. Abstr.*, 1959, **6**, 510) is added, and the soln. is diluted to 50 ml. After 20 min. the extinction of the bluish-pink soln. is measured with a red filter.

G. S. SMITH

3143. **Amperometric titration of magnesium with ammonium ferrocyanide.** V. M. Babenȳshev and A. I. Blesnova (Kuĭbȳshev Ind. Inst.). *Zhur. Anal. Khim.*, 1959, **14** (6), 682–685.—To the soln. of $MgCl_2$ (pH 6 to 9) add 25 ml of ethanol (96%), dilute to 50 ml, and titrate with 0·1 *M* $(NH_4)_4$-$Fe(CN)_6$ with the use of a rotating platinum electrode. The titration curve is in the form of an obtuse angle; the end-point is determined graphically. Negative errors (> 2%) are obtained, probably because of the slow pptn. of Mg towards the end of the reaction. Aluminium and Be do not interfere, but alkali metals in excess do. Ions that are pptd. by $[Fe(CN)_6]^{4-}$ (*e.g.*, Fe^{3+}, Cu^{2+}, Mn^{2+} and Zn^{2+}) interfere but, in the presence of small amounts of these ions, the error is not increased and may even be reduced owing to compensation of the usual negative error.

C. D. KOPKIN

3144. **Determination of microgram quantities of magnesium in mineralised tissues.** H. G. McCann (Nat. Inst. Dental Res., Nat. Inst. Health, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2091–2092.—From 0·2 to 3% of Mg in a sample (1 to 10 mg) containing large amounts of calcium phosphate can be determined, in alkaline soln., by chelation of the Ca with EDTA and then determining the Mg directly as the Thiazole Yellow (Titan yellow) lake at 548 mμ in a vol. of 50 ml. The concn. of Ca must be kept approx. the same (3·6 mg) in all soln., otherwise some Mg will be complexed. The sample (bone, dentine, enamel) must initially be completely ashed at 600°; any Zn present must be removed with dithizone in $CHCl_3$ at pH 5. The accuracy is equiv. to that of the gravimetric method.

W. J. BAKER

3145. **Determination of small amounts of aluminium in metallic magnesium by a luminescence method.** A. F. Fioletova. *Zhur. Anal. Khim.*, 1959, **14** (6), 739–740.—*Procedure*—Moisten 0·2 g of metallic magnesium in a 50-ml quartz beaker with 5 ml of water and dissolve it in 6 *N* HCl, added dropwise. Evaporate the soln. to a syrup, cool, add 10 ml of 6 *N* HCl, transfer the soln. to a 50-ml quartz separating-funnel, add 10 ml of diethyl ether and shake vigorously for 3 to 5 min. Set aside for 10 min., run the aq. phase into the original beaker and the ether phase into a beaker containing a few crystals of KSCN and 1 ml of water. Repeat until the ether extract gives no reaction for Fe. Again evaporate the aq. soln. to a syrup, cool, dissolve the residue in water and transfer the soln. to a 200-ml quartz flask; add the washings of the beaker and funnel, make up to vol. and mix. Transfer 10 ml of the resulting soln. into a quartz separating-funnel and add 1 ml of 8% $NaHCO_3$ soln. (freed from Al by shaking with a 2% soln. of 8-hydroxyquinoline in $CHCl_3$). Add 1 ml of a 2% soln. of 8-hydroxyquinoline in *N* acetic acid and 5 ml of $CHCl_3$, shake vigorously for 5 min. and set aside for 5 min. Transfer the $CHCl_3$ layer to a 10-ml quartz tube, repeat the $CHCl_3$ extraction and make up to vol. with $CHCl_3$. Prepare a standard extract with the expected amount of Al in the same way. Irradiate the $CHCl_3$ extracts with u.v. light and compare the intensities of the fluorescence. Add the amount of Al found to a soln. of Mg from which Al has already been extracted, and use this as standard; if the intensities of luminescence do not coincide, adjust the standard amount of Al and repeat. Parts per thousand of Al can be determined with a mean error of ±14%; Ca, Cr, NO_3^- and SO_4^{2-} do not interfere.

C. D. KOPKIN

3146. **Fluorimetric study of the magnesium - NN′-di-(salicylidene)ethylenediamine system.** C. E. White and F. Cuttitta (Univ. of Maryland, College Park, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2083–2087.—Magnesium ions react with NN′-di-(salicylidene)ethylenediamine in slightly alkaline dimethylformamide soln. to form a highly fluorescent complex, which shows max. fluorescence excitation at 355 mμ and an emission max. at 439 mμ. The complex has a metal to ligand ratio of 1:1, and the method is sensitive to 7×10^{-6} μmole of Mg per ml. The analysis of samples from the Bureau of Standards showed good correlation of results by this fluorimetric method and spectrophotometric methods.

G. P. COOK

3147. **Spectrophotometric study of the magnesium - NN′-di-(salicylidene)ethylenediamine system.** F. Cuttitta and C. E. White (Univ. of Maryland, College Park, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2087–2090.—Magnesium reacts with NN′-di-(salicylidene)ethylenediamine in dimethylformamide soln. to yield a yellow complex that gives max. absorption at 355 mμ when the soln. contains 0·25 ml of 0·5 *M* *iso*butylamine per 25 ml. Beer's law is obeyed and $3{\cdot}8 \times 10^{-4}$ μg of Mg can be detected if a 5-cm light path is used. The complex has a ligand to metal ratio of 1:1 and a molecular extinction coeff. of 13,450. The standard deviation is < ± 1%.

G. P. COOK

3148. **Use of Unithiol [sodium 2:3-dimercaptopropanesulphonate] as a masking agent in the complexometric determination of calcium and magnesium.** L. A. Vol'f (S. M. Kirov Leningrad Textile Inst.). *Zavod. Lab.*, 1959, **25** (12), 1438–1439.—The reagent gives complexes with Hg^{2+}, Pb^{2+} and Zn^{2+} that are stable in the presence of EDTA and permits the complexometric determination of Ca and Mg in their presence. The soln. is treated with 10 to 20 ml of 0·25% Unithiol soln., 5 ml of a buffer soln. (350 ml of 25% aq. NH_3 and 54 g of NH_4Cl per litre), and 10 drops of an ethanolic 0·4% soln. of Eriochrome black T, then diluted to 100 ml and titrated with 0·01 *N* EDTA (disodium salt).

G. S. SMITH

3149. **Use of sucrose solution for the determination of "available CaO" in commercial lime.** E. Walsh, B. F. Wright and J. B. Alexander. *S. Afr. Sug. J.*, 1959, **43**, 61–63.—Data are presented indicating the unreliability of available CaO determinations based on lime extractions with sucrose. Interferences are shown to be due to the presence of traces of reducing sugars such as fructose and glucose and of soluble Mn. In all cases the sucrose method gave a lower value than the phenol method.

CHEM. ABSTR.

3150. **Flame-photometric determination of strontium in minerals low in strontium.** H. Gundlach (Bundesanst. f. Bodenforsch., Hanover, Germany). *Z. anal. Chem.*, 1959, **171** (1), 9–22.—The insoluble residue and SiO_2 are separated from a 0·1 to 1·0-g sample (*e.g.*, of calcite, dolomite, barytes or silicate) by standard methods and the Sr in 0·9% HCl soln.

is measured at 460·7 and 466 mμ; the difference between the measurements gives the Sr concn. Interferences by Ca, Ba, Mg, Fe, Al and Mn are eliminated by the procedures described, and the effect of alcohols, ethers, ketones and org. acids on the increase of the Sr emission in the flame has been examined. The relative accuracy of the method is ± 5%, but may reach ± 10% with very impure minerals. B. B. BAUMINGER

3151. **Complexometric titration (chelatometry). XLV. Selective determination of zinc in slightly acid medium with xylenol orange and methylthymol blue.** I. Janoušek and K. Študlar (Leninovy Závody, Plzeň, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3799–3801 (in German).—*Procedure*—To the soln. of Zn^{2+}, in the presence of Cu, Ni, Co, Hg, Al, Ca, Mg and Ag, add NaF to mask Al (3 to 5 ml of 4% soln. for each 10 mg of Al) and dilute with H_2O to about 150 ml. Add aq. NH_3 till slightly alkaline and solid KCN till the soln. is decolorised or till the ppt. is dissolved. Add a suitable amount of xylenol orange or methylthymol blue as indicator and HCl soln. (1:1) dropwise till yellow. Add acetate buffer soln. (pH 6 to 6·1) and titrate with EDTA (disodium salt) soln. Zinc (16·35 mg) was determined in the presence of 100 mg of Cu, Ni and Mg, 50 mg of Co and Al, and 30 mg of Ca, with an error of ± 1%. J. ZÝKA

3152. **Complexometric determination of zinc in concentrates with the indicators xylenol orange and methylthymol blue.** O. B. Budevskiĭ, A. N. Karolev, R. A. Karanov and L. Simova-Filippova (Sci. Res. Inst. for Metallurgy and Useful Minerals, Sophia). *Zavod. Lab.*, 1959, **25** (12), 1439–1441.—Titration is carried out at a pH between 5·3 and 5·8 after removal of interfering elements. G. S. SMITH

3153. **Quantitative determination of zinc and cadmium.** E. A. Bozhevol'nov, V. M. Dziomko and G. V. Serebryakova. USSR Pat. No. 120,029; 21.5.59.—The method is based on the green fluorescence shown by u.v. irradiation of the complexes of Zn and Cd with 8-toluene-*p*-sulphonamidoquinoline (**I**) at pH 8·0 to 8·3 (glycine buffer). (The complexes can be extracted with $CHCl_3$, the intensity of the fluorescence increasing, but **I** itself then fluoresces.) The sensitivity is 0·1 μg of Zn or Cd in 5 ml of soln., or 0·01 μg of Zn or Cd in 5 ml if the aq. soln. is extracted with 0·4 times its vol. of $CHCl_3$; the limiting dilution is 1 in 10^6. The fluorescence is not quenched by the presence in 5 ml of soln. of 500 μg of Na, K, Th, Cs, Cr, Pd, Ba, Sr, Sb^V, U, Ce, Nd or Ag or 50 μg of Be, Mo, Mg, Rb, Ru, Se or Pb; only Co, Ni and Te interfere at concn. of 5 μg in 5 ml. The complex with Al does not itself fluoresce, even at concn. of Al of 500 μg in 5 ml, but 50 μg in 5 ml quenches the fluorescence of the Zn and Cd complexes. The method is illustrated by determining total Zn and Cd in high-purity hydrobromic acid. C. D. KOPKIN

3154. **Separation of boron from alloys and other materials by pyrohydrolysis.** V. R. Wiederkehr and G. W. Goward (Westinghouse Electric Corp., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2102–2103.—Boron can be completely separated from Zr, Zircaloy, Zircaloy-base uranium alloy, stainless steel or boron carbide, by pyrohydrolysis with steam (1 to 3 ml per min.) in a nickel tube at 1100° for 90 min. The distillate, which is completely free from interfering elements, is collected in ≃ 20 ml of H_2O kept slightly alkaline, and the B is determined by any of the usual methods. Because the procedure is adapted to remote control, it can be used to isolate B from radioactive matrices. W. J. BAKER

3155. **Analysis of pentaborane.** A. F. Zhigach, E. B. Kazakova and R. A. Kigel'. *Zhur. Anal. Khim.*, 1959, **14** (6), 746–747.—The method is based on the quant. reaction of B_5H_9 with ethanol to form hydrogen and triethyl borate, which is easily hydrolysed by water to boric acid. Suitable apparatus for the treatment of the sample (0·1 to 0·2 g) at 0° in N, and for the measurement of the vol. of H liberated, is illustrated. The residual reaction mixture is made up to a known vol. with water, an aliquot is neutralised with 0·1 *N* NaOH to methyl red, then 30 ml of glycerol, invert sugar syrup or mannitol soln. is added, and the mixture is titrated, with phenolphthalein as indicator. C. D. KOPKIN

3156. **Thermal stability and titrimetric determination of decaborane [decaboron tetradecahydride].** M. I. Fauth and C. F. McNerney (Res. and Devel. Dept., U.S. Naval Propellant Plant, Indian Head, Md., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 91–93.—This compound is stable in air up to 125° and in He up to at least 150°. The material may be assayed by dissolution in glacial acetic acid, addition of excess of KIO_3 and iodimetric determination of this excess. A standard deviation of ±0·37 is reported for 10 determinations on a sample assaying at 98%. T. R. ANDREW

3157. **Detection of aluminium ions with 5-hydroxy-1:4-naphthaquinone (juglone).** L. N. Alzenberg (Kishinev Agric. Inst.). *Zhur. Anal. Khim.*, 1959, **14** (6), 741–742.—An ethanolic soln. of juglone gives a purple-red colour with Al^{3+}. The most intense colour is obtained at pH 3·0 to 3·5 for $AlCl_3$ and pH 2·35 to 9·90 for $Al(NO_3)_3$; the detectable minimum is 162 μg of Al in 2 ml of $Al(NO_3)_3$ soln. and the limiting dilution is 1 in $2·4 \times 10^4$. C. D. KOPKIN

3158. **High-frequency titration of aluminium.** F. Pungor and E. É. Zapp (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest). *Z. anal. Chem.*, 1959, **171** (3), 161–172 (in German).—The direct titration of $AlBr_3$ and $Al_2(SO_4)_3$ with NaOH, $Ba(OH)_2$, triethylamine and aq. NH_3 soln. is discussed; triethylamine gives the best results but the titration is slow. The most rapid and reliable method is to add excess of $Ba(OH)_2$ soln. to the acidified test soln. and back-titrate with dil. acetic acid. P. D. PARR-RICHARD

3159. **New rapid determination of aluminium in copper alloys.** E. Mohr (V.E.B. Berliner Metallhütten- u. Halbzeugwerke, Berlin). *Chem. Tech., Berlin*, 1959, **11** (11), 598–599.—The separation of Al from interfering ions (Cu, Pb, Fe, Ni, Sb, Sn, Mn, Zn and Mg) is obviated by masking them with NaCN and EDTA at pH 9 to 10; Al is then pptd. with 8-hydroxyquinoline and determined with KBr-$KBrO_3$ soln. The method takes 20 min. and has good reproducibility. It is suitable for alloys containing ≯ 20% of Al and also (by the use of more NaCN) for zinc alloys. With copper alloys, the soln. remaining after the iodimetric determination of Cu may be used for determining Al. *Procedure*—Dissolve the sample (≃10 mg of Al)

in dil. HNO_3, boil off nitrous fumes, and dilute to 100 ml with hot water. Add satd. $Na_2S_2O_3$ soln. (5 ml) and then 25 ml of the masking soln. (100 g of NaCN, 50 g of EDTA, and 300 ml of conc. aq. NH_3 diluted to 1 litre; stable for 8 days). Then precipitate the Al with 4% 8-hydroxyquinoline soln. (10 ml) at the b.p. and stir till the ppt. has coagulated (15 sec.). Collect the ppt. after 1 min., wash it and dissolve it in hot HCl (20 ml). Cool, add 0·1 *N* KBr - $KBrO_3$ from a burette until one drop decolorises methyl orange, add 5% KI soln. (10 ml), and titrate the liberated iodine with 0·1 *N* $Na_2S_2O_3$. J. P. STERN

3160. **Spectrographic analysis of seam weldings of aluminium - magnesium alloys.** A. S. Dem'yanchuk and O. P. Ryabushko. *Avtomat. Svarka*, 1959, (3), 69–73; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,349.—Analyses were carried out on a series of standard samples. The spectra were excited by a high-frequency spark-discharge, with a primary current of 0·8 amp., a secondary voltage of 4000 V and a gap of 1·8 mm. A graphite rod in the form of a truncated cone (diam. of the top flat surface, 2 mm) served as a stationary electrode. The spectra were photographed in an ordinary quartz spectrograph, with exposure for 40 sec. The analytical lines used (in A) and concn. ranges (%) of metals (in seams) were Mg 2779·8 (1·0 to 10), Mn 2949·2 (0·10 to 2), Si 2516·1 (0·10 to 2), Fe 2599·4 (0·1 to 2), Cu 3247·5 (0·05 to 1), and Ti 3088·0 (0·05 to 0·5); the standard line was Al 2632·4. The intensity of the Mg and Mn lines was higher when a graphite electrode was used than with copper or aluminium electrodes. The graphite electrode decreases the oxidation of Mg and Mn in the "sparked" area, brings them more uniformly and completely into the discharge "vapour," and increases both absolute and relative intensity of the lines of the internal standard. While investigating the effect of the structures of samples it has been shown that the discrepancy in the determination of Mg, Mn, Si and Fe in aluminium - magnesium alloys is not higher than the experimental error; this permits the use of test and standard samples of different structure. It has been observed that Mg does not interfere with the determination of Fe and Mn. The remaining elements (Si, Cu and Ti) did not affect the results. The average analytical error was ± 4%. W. ROUBO

3161. **Determination of magnesium and calcium in crude aluminium and argillaceous materials (bauxite).** A. S. Andreev, A. Marshikova and G. V. Telyatnikov. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 51–55; *Ref. Zhur., Khim.*, 1960, (3), Abstr. No. 8847.—*Procedure for Mg in crude aluminium*—Dissolve the sample in 20% NaOH soln., add 10% Na_2CO_3 soln. (10 ml) and 3% H_2O_2 soln. (1 ml) and boil. Cool, filter off the ppt. containing $CaCO_3$ and $MgCO_3$, wash it with an alkaline soln. (3% of Na_2CO_3 and 5% of NaOH), and dissolve it in HCl (1:3) (20 ml) in the presence of 3% H_2O_2 soln. (2 ml). Remove interfering cations as pyridine - thiocyanate complexes (Andreev *et al.*, *Anal. Abstr.*, 1960, **7**, 3269). To an aliquot of the residual soln. add 5% sucrose soln. (1 ml), 5% hydroxyammonium chloride soln. (1 ml), 0·05% Titan yellow soln. (0·5 ml) and 2 *N* NaOH (1 ml); dilute to 50 ml and determine Mg photometrically with a green filter. *Procedure for Mg and Ca in argillaceous materials*—Two procedures may be used. (*i*) Fuse the sample with twice its weight of Na_2CO_3. Leach out the melt with HCl soln., separate SiO_2 by dehydration and the excess of Al with NaOH and Na_2CO_3. (*ii*) Fuse the sample with NaOH and Na_2CO_3, and leach out the melt with water; Al and SiO_2 dissolve. In the case of (*i*), continue the analysis as described above, determining Mg alone, and the sum of Mg and Ca complexometrically, and obtaining Ca by difference. In the case of (*ii*), either dissolve the residue in HCl and separate interfering ions by the usual methods, or suspend the residue in water, and pass CO_2 until the $CaCO_3$ and $MgCO_3$ are brought into soln. as bicarbonates. Then determine Ca by the oxalate method and Mg with 8-hydroxyquinoline. K. R. C.

3162. **Activated alumina for use as desiccant for packages.** British Standards Institution (2 Park St., London, W.1). B.S. 2541 : 1960. 12 pp.—Tests are given for moisture, pH, ammonia and ammonium compounds, water-soluble chlorides and sulphates, and absorptive capacity.

3163. **Dissolution of fused aluminium oxide and the determination of impurities.** N. G. Mendlina, A. A. Novoselova and R. S. Rŷchkov. *Zavod. Lab.*, 1959, **25** (11), 1293–1294.—Dissolution of fused Al_2O_3 is rapid in mixtures of H_3PO_4 and H_2SO_4 or H_3PO_4 and HCl. With the former, 1 g is heated for 20 to 35 min. with 8 to 10 ml of H_3PO_4 (sp. gr. 1·45) and 14 to 15 ml of H_2SO_4 (sp. gr. 1·17) at 150° to 180°. With the latter, the sample is heated for 20 to 25 min. with H_3PO_4 alone and then for 1 hr. with conc. HCl (2 × 10 ml). To determine Ca and Mg, the excess of acid is removed by evaporation with water (2 × 5 to 10 ml) and the salts of Al are hydrolysed by boiling with 250 to 300 ml of water. The filtered soln. is evaporated to a vol. of 10 ml and Mg and Ca are pptd. as phosphates. The ppt. is dissolved in HCl, and Ca and Mg are determined by titration with EDTA (disodium salt). G. S. SMITH

3164. **Quantitative determination of gallium.** E. A. Bozhevol'nov, A. M. Lukin and M. N. Gradinarskaya. *Avtomat. Svarka SSSR*, 1959, No. 116,838; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,357.—A highly sensitive fluorimetric method for the determination of Ga, based on the application of 5-chloro-2-hydroxy-3-sulphophenylazoresorcinol (**I**) as fluorimetric indicator, has been evolved. The sensitivity is ≃ 0·01 μg of Ga in 5 ml of test soln. when determining Ga in aq. soln., and 0·005 μg of Ga in 5 ml of aq. test soln. when determining Ga after extraction with *iso*amyl alcohol (the ratio of aq. and org. phases being 10:1). There is no interference from Al^{3+} (100 times the Ga content), Li^+, Na^+, K^+, Cs^+, NH_4^+, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Be^{2+}, Mg^{2+}, phthalates or citrates at concn. of 50 μg in 5 ml; Sn, Zr or Pr at concn. of < 5 μg in 5 ml; or Cu, Fe, U or Mo at concn. of < 0·5 μg in 5 ml. *Procedure*—To 30 ml of the test soln. add an equal vol. of phthalate buffer (pH 2), mix well and divide the mixture into three equal portions. To one add 0·2 μg of Ga, to the second 2 drops of 0·05 *M* EDTA and to all three 0·25 ml of 0·01% soln. of **I**. Set aside for 3 hr. and then measure the intensity of the fluorescence of the three solutions. Calculate the amount of Ga by the usual method. When the Ga content is < 0·01 μg in 5 ml then add 0·02 μg of Ga to the control sample and measure the intensity of the fluorescence of the *iso*amyl alcohol extracts (2·5 ml of *iso*amyl alcohol should be used). W. ROUBO

3165. **Present state of the analytical chemistry of gallium, indium and thallium.** T. V. Cherkashina and V. M. Vladimirova. *Zavod. Lab.*, 1959, **25** (11), 1307–1318.—A review, with 118 references, is presented. G. S. SMITH

3166. **Flame-photometric determination of gallium, indium and thallium.** H. Bode and H. Fabian (Anorg.-chem. Inst., Tech. Hochschule, Hannover, Germany). *Z. anal. Chem.*, 1959, **170** (2), 387–399.—The addition of water-miscible organic solvents to the spray soln. used for flame photometry causes a considerable increase in sensitivity. In particular, the use of a 0·5 *N* HCl soln. containing 80% by vol. of acetone gives a 50-fold increase in sensitivity for Ga, In and Tl. Few elements interfere if suitable corrections are made for background radiation, and all interference can be eliminated by using an ether-extraction step before flame photometry. Extraction procedures and examples are given for the determination of Ga in a number of synthetic and natural aluminium and zinc ores. W. T. CARTER

3167. **Study of the behaviour of complex compounds of indium, zinc and cadmium in ammonium carbonate solution on ion-exchange resins.** I. P. Alimarin, E. P. Tsintsevich and V. P. Burlaka (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1959, **25** (11), 1287–1290.—The complex carbonate of In is adsorbed by the anionite EDE-10P, but passes completely into the percolate from the cationite KU-2. By means of EDE-10 Pit is possible to separate In from Zn with relative concn. between 1:1 and 1:1000, and by means of KU-2 it is possible to separate In from Cd with relative concn. between 20:1 and 1000:1, and In from Al with relative concn. between 4:1 and 1000:1. G. S. SMITH

3168. **Colour reactions for scandium.** I. M. Korenman, V. P. Gunina and L. K. Trifonova (N. I. Lobachevskiĭ Gorki State Univ.). *Zhur. Anal. Khim.*, 1959, **14** (5), 547–549.—Colour reactions for Sc with hydroxyanthraquinones and 1:1′-dihydroxy azo dyes are studied, with particular reference to their use at low pH values. Of the former, the most sensitive reagents are Alizarin red S (**I**) (pH 1 to 5); 1:4-dihydroxyanthraquinone (**II**) (pH 5 to 11); 1:2:4-trihydroxyanthraquinone (**III**) (pH 2 to 7); and Anthracene blue WR (C.I. Mordant blue 32) (pH 3 to 5). **I** (at pH 1 to 3) and **III** (at pH 2 to 3) can detect Sc in the presence of a 50-fold amount of Y, La, Ce and Al; **II** can detect Sc at pH 6 to 9 in the presence of a 70-fold amount of Th, Y, La and Ce, which give with **II** an orange colour; Fe^{III} interferes in these reactions. Similar data are given for 1:1′-dihydroxy azo dyes that give colour reactions with Sc at low pH values; the most useful are Acid chrome blue black K, Acid monochrome green S, Acid monochrome blue Z and Acid chrome black S.

C. D. KOPKIN

3169. **Colorimetric determination of scandium.** V. G. Brudz', D. A. Drapkina, K. A. Smirnova, V. I. Titov, I. E. Pokrovskaya, E. P. Osiko, N. I. Doroshina and V. I. Maslinikova. USSR Pat. No. 119,709; 10.5.59.—The reagent is "sulphonazo," di-[3-(8-amino-1-hydroxy-3:6-disulpho-2-naphthylazo)-4-hydroxyphenyl] sulphone, (**I**). An aq. 0·001% **I** soln. of pH 5·0 is blue-pink in colour, changing to violet or blue-violet in the presence of Sc. The visual or standard colorimetric series method may be used to determine Sc; 0·2 to 10 μg of Sc in 5 ml of soln. (pH 5·0 to 5·4, buffered with acetate or hexamine) can be determined. Alkali metals, alkaline-earth metals, the rare-earth metals, Y, Al, Be, Zn, Cd, Ge and Pb do not interfere. Elements that are hydrolysed under the reaction conditions (Fe, Ti, Zr) interfere. Intensely coloured compounds with **I** are given by V, Ga, In and Co, and less strongly coloured compounds by U, Th, Zr, Hf, Ni, Bi and Al. To determine Sc in soln. containing $\geq$ 100 μg of Sc and free from interfering metals and excess of acid, add a saturated soln. of hexamine (**II**) or 5 ml of buffer soln. of pH 5·0 (a mixture of **II** and HCl) and add 2 ml of 0·02% **I** soln. Make up to 25 ml, and after a few minutes measure the extinction in a 20-mm cell at 610 mμ, using a calibration curve for the content of Sc. To determine Sc in rocks and minerals, decompose 1 g of sample with acid or by alkaline fusion, remove silicic acid, and precipitate Sc with ammonium tartrate in the presence of Y as carrier. Set aside overnight, filter off the tartrates, wash them and ash. Dissolve the residue in dil. HCl, add 5 ml of 0·1 *M* acetate buffer soln. of pH 5·0, and proceed as above, using 3 ml of 0·03% **I** soln. If the Fe or Al contents in the sample are > 20%, they are removed before the tartrate pptn., Fe by extraction with diethyl ether from the HCl soln., and Al by pptn. of $Al(OH)_3$ with 1% NaOH soln. Amounts of Ti and Zr > 10% must be first extracted as cupferronates with $CHCl_3$. **I** may be used as a cationic indicator in the complexometric determination of Sc. The preparation of **I** is described. C. D. KOPKIN

3170. **Determination and separation of scandium by means of N-benzoylphenylhydroxylamine.** I. P. Alimarin and Tszé Yun'-Syan (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1959, **25** (12) 1435–1437.—The reagent *N*-benzoylphenylhydroxylamine (*cf.* Shome, *Analyst*, 1950, **75**, 27) precipitates Sc completely at a pH of 5·4. Ignition at 600° gives Sc_2O_3. The complex is sol. in *n*-butanol, amyl acetate, benzene and other organic solvents. To separate Sc from the rare-earth elements, the acid soln. (100 ml) is treated with 30 ml of 20% ammonium acetate soln. and a few ml of acetic acid and then with the reagent, the ppt. is collected and washed with water, dried, ignited and weighed, and the filtrate is treated with aq. NH_3 to precipitate the rare-earth elements, which are collected and ignited at 800° to 900°. In 3 *N* HCl, Zr, but not Sc, is pptd. by the reagent; from 1 to 8 *N* HCl, Zr, and from 5 to 10 *N* HCl, Ti, are completely extracted by *iso*amyl alcohol, whereas Sc is not extracted. At pH $\simeq$ 4·5 Sc is extracted, but the rare-earth elements are not extracted. Extractions can be carried out with a 3% soln. of the reagent in *iso*amyl alcohol. G. S. SMITH

3171. **Complexometric determination of scandium.** B. S. Tsŷvina and O. V. Kon'kova (State Sci. Res. and Development Inst. of the Rare Metals Industry). *Zavod. Lab.*, 1959, **25** (12), 1430–1435.—At a pH of 2·6, and with murexide as indicator, Sc can be determined complexometrically in the presence of other elements, except Cu, Ni, Fe, Th and Zn. Separation of Sc and Th by the tartrate or the benzosulphinate method is unsatisfactory, but the iodate method is applicable if a correction is applied. To determine Sc in the presence of < 1 mg of Th, a soln. containing $\geq$ 10 mg of total rare-earth elements and 5 mg of Ti is neutralised to Congo red paper with aq. NH_3 (1:3), then mixed with 10 ml of a buffer soln. containing 35 g of Na acetate and

35 ml of conc. HCl in 2 litres, and diluted to 50 ml. The soln. is titrated in the presence of murexide - NaCl (1:100) as indicator with 0·05 *M* EDTA (disodium salt) to the transition from yellow to violet - pink. In the presence of larger amounts of Th, the soln. in HCl is evaporated with 10 to 15 ml of conc. HNO_3 to a vol. of 5 ml, water (10 ml) is added, and the soln. is slowly mixed with 15 ml of a 10% soln. of KIO_3 in HNO_3 (1:2) and then with 30 to 40 ml of 0·8% KIO_3 soln. containing 50 ml of HNO_3 per litre. After 15 min. on a boiling-water bath, with occasional stirring, the ppt. is washed by decantation and then washed on a filter with 0·8% KIO_3 soln. containing 50 ml of HNO_3 per litre. It is then dried, ashed and weighed. The filtrate is neutralised with aq. NH_3 and HCl, and the slightly acid soln. is boiled for 5 to 10 min. and then treated with aq. NH_3 (1:1) in the presence of phenol red indicator so that there is an excess of 1 ml of aq. NH_3 (1:1). The soln. is boiled, and the ppt. is collected and washed with ammoniacal 2% NH_4Cl soln. until it is free from sol. iodate. It is then dissolved in 10 to 15 ml of HCl (1:3), the diluted soln. is treated with KI, the iodine liberated is boiled off, the soln. is diluted to 100 ml and an aliquot is titrated as described above. A correction is made for Sc co-pptd. with Th. When the total amount of Sc is between 10 and 50 mg the number of mg of Sc per mg of the Th ppt. increases linearly from 0·020 to 0·031. G. S. SMITH

3172. **Back-titration with mercuric nitrate in alkaline medium. Estimation of small amounts of lanthanum and analysis of its binary mixtures with some other metals.** H. Khalifa, M. Hamdy and A. Soliman (Micro-anal. Chem. Dept., Nat. Res. Centre, Dokki, Egypt). *Z. anal. Chem.*, 1959, **171** (3), 178–185 (in English).—The determination of La, alone or with another cation, by addition of an excess of EDTA and potentiometric back-titration at pH 8 to 11 with $Hg(NO_3)_2$ soln. is described. *Procedure for lanthanum and barium*—Titrate at pH 10·5 to 11 for La plus Ba, then titrate La at pH 8; Sr or Mg cannot be determined in this way. *Lanthanum and thorium*—Titrate La plus Th; for La alone, precipitate Th by boiling with benzoic acid and a little aniline and determine La in the filtrate. *Lanthanum and other cations*—After masking La (0·1 to 5 mg) with NH_4F, titrate Ni, Co, Zn, Cd, Cu, Bi or Mn^{II}; the sum of the two cations is obtained by titrating in the absence of NH_4F.
P. D. PARR-RICHARD

3173. **Separation of the lanthanides at amalgam cathodes. III. Electrochemical fractionation of the lanthanides at a lithium amalgam cathode.** E. I. Onstott. *J. Amer. Chem. Soc.*, 1959, **81** (17), 4451–4458.—Respective electrolysis of monazite, an yttrium earth and a Tb - Dy mixture at a lithium amalgam cathode showed particular rates for individual lanthanides, the relative ease of electrolysis being in the order—Eu, Yb, Sm, La, and other elements according to their atomic number; the rate of electrolysis for Y was between those for Er and Tm. Separations are predictable from the relative rates. METALLURG. ABSTR.

3174. **The characterisation and identification of the rare-earth-chloride hydrates by differential thermal analysis.** W. W. Wendlandt and J. L. Bear (Technol. Coll., Lubbock, Tex., U.S.A.). *Anal. Chim. Acta*, 1959, **21** (5), 439–442.—The thermograms of all the rare-earth-chloride hydrates (except those of Pm) are shown, and their value for the identification of separate rare-earth elements or, in some instances, mixtures thereof, is briefly discussed. The curves can be classified in four groups, mainly according to the position and maxima of the endotherms—La, Ce, Pr and Nd; Sm, Eu and Gd; Tb, Dy, Y, Ho, Er and Tm; and Yb and Lu. W. J. BAKER

3175. **Rapid photometric determination of total rare-earth elements.** A. F. Kutelnikov and G. A. Lanskoi (All-Union Inst. of Mineral Raw Materials, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (6), 686–690.—With all rare-earth metals arsenazo (**I**) gives violet soln. which have max. absorptions in the range 540 to 560 mμ. The optimum pH range is 6·0 to 7·5. The molar extinction coeff. range from $\simeq 2{\cdot}4 \times 10^4$ at 580 mμ to $\simeq 1{\cdot}4 \times 10^4$ at 600 mμ, and the complexes contain **I** and the metal in the ratio of 1:1. To determine total rare-earth metals, dissolve the mixed oxides or sulphates in the minimum amount of HCl, adding H_2O_2 if necessary, and make up to a known volume; transfer an aliquot to a 25-ml flask, neutralise with hexamine, add 2 ml of a 0·1% **I** soln., make up to volume and measure the extinction with a liquid filter (8% $K_2Cr_2O_7$ soln. + 2% $CuSO_4$ soln. in a 2-cm cell, or 10% $K_2Cr_2O_7$ soln. + 1% $CuSO_4$ soln. in a 5-cm cell). Construct a calibration curve with $Ce(NO_3)_3$; a rectilinear graph is obtained. Thorium gives a similar reaction with **I**; the extinction of the resulting complex is measured at pH 1·6 to 1·8 (at which the rare-earth metals do not give coloured soln.) and the rare-earth metals are obtained by difference. Interference by Al and Fe^{III} is eliminated by adding Na sulphosalicylate (2 to 3 ml of 25% soln. in 25 ml) and ascorbic acid (0·1 to 0·2 g per 100 ml of soln.). C. D. KOPKIN

3176. **Flame-spectrophotometric determination of some rare-earth elements.** N. S. Poluéktov and M. P. Nikonova. *Ukr. Khim. Zhur.*, 1959, **25** (2), 217–225; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,303.—The determination of rare-earth elements by their excitation in an air - acetylene flame has been studied. It has been shown that La, Eu, Y and Yb can be determined in the total oxides and in compounds containing a number of different rare-earth elements, and that the addition of NH_4Cl to a test soln. increases the intensity of the excitation of these elements (owing probably to the formation of volatile chlorides). A method for the determination of La, Eu, Yb and Y, based on the comparison of the heights of the peak maxima of molar bands (La, Y) and spectral (atomic) lines (Eu, Yb), has been developed. The sensitivity of the method is 0·2% (for La_2O_3), 0·03% (Eu_2O_3), 0·003% (Yb_2O_3) and 0·03% (Y_2O_3), with a relative error of ± 7%. The actual determination takes $\simeq$ 10 min.; the upper determinable range is 10 to 30% of R_2O_3 in total oxides. W. ROUBO

3177. **Separation of metal ions by means of ion-exchange membranes. I. Separation of rare-earth mixtures, and of thorium - rare-earth mixtures with EDTA.** K. Bril, S. Bril and P. Krumholz. *J. Phys. Chem.*, 1959, **63** (2), 256–259.—The separation of metal ions by electro-migration in partially complexed soln. is described. Ion-exchange membranes and EDTA as the complexing agent are used. Good separation is obtained for mixtures of La, Pr and Nd as well as of Th and Nd. The separation is affected by the nature of the accompanying ions. The influence of ClO_4^-, Cl^-, NO_3^- and acetate is studied. METALLURG. ABSTR.

3178. **Quantitative determination of ytterbium in the presence of large quantities of erbium by oscillographic polarography.** Ya. P. Gokhshtein and G. A. Kutyreva (V. I. Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (6), 691–695.—Ytterbium cannot be determined by normal polarography in the presence of Er. For oscillographic polarography, dissolve 200 to 700 mg of Er_2O_3 containing Yb in 5 ml of conc. HCl, evaporate almost to dryness, dissolve the residue in water and transfer the soln. to a 10- or 20-ml flask. Add a few drops of conc. aq. NH_3, and adjust the NH_4Cl concn. to 0·1 *N* and the pH to 4. Transfer 1 ml of the soln. to the electrolyser, apply a constant potential of −1·0 V and record the oscillogram with a single trace of known amplitude (≃ 0·8 V) and a drop-time of about 1 sec. Record the oscillograms of the background and soln., determine the diffusion current and calculate the concn. of Yb. With < 0·1% of Yb the sensitivity of the method is greater than that of the X-ray spectrographic method; the error is ⩾ 11%. With > 0·1% of Yb the two methods give results which are in good agreement.

C. D. KOPKIN

3179. **Use of oscillographic polarography in quantitative analysis. X. Determination of europium in the presence of other rare-earth elements.** J. Doležal and K. Janáček (Dept. of Anal. Chem., Charles' Univ., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3790–3792 (in German).—In soln. of certain anions, rare-earth metals are characterised by cut-ins at ≃ − 1·4 V, but in a medium of thiocyanate or nitrate, only Eu^{III} produces two characteristic cut-ins. The cathodic cut-in at −0·9 V and the anodic one at −0·30 V (in *N* KNO_3) are suitable for analytical use.

J. ZÝKA

3180. **Spectrographic determination of silicon in uranium - silicon alloys.** G. Baudin and J. Ernoult (Centre d'Études Nucl., Grenoble). *Compt. Rend.*, 1959, **249** (22), 2321–2323.—The sample is converted into a mixture of SiO_2 and U_3O_8 by placing it in a cold furnace and slowly raising the temp. to 900°, which is maintained for 30 min. The finely powdered mixture of oxides (100 mg) is mixed with graphite (580 mg) and Mn_3O_4 (50 mg), the Mn_3O_4 serving as the internal standard. This mixture is placed in the bore of an upper brass electrode (illustrated) and excited by sparking, with a preburn of 5 sec., an exposure of 1 min., and a lower graphite counter-electrode. The lines used are Mn 2527·4 A and Si 2524·1 A. The method is applicable over the range from 0·5 to 25% of Si, with a coeff. of variation of 6·3% (20 exposures).

R. E. E.

3181. **Neutron activation analysis of silicon carbide.** L. Flowe, H. D. Thompson and J. P Cali (Air Force Cambridge Research Center, Bedford, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1951–1953.—A method is described for determining impurities in the parts per 10^9 range or less. After irradiation with thermal neutrons the sample is decomposed with chlorine and oxygen at 1250°. Standard radiochemical procedures are then used for separating and measuring the induced activities. Inconsistencies found in analyses are much greater than the uncertainty of the measurements and indicate a non-homogeneous distribution of impurities.

K. A. PROCTOR

3182. **Silica gel for use as desiccant for packages.** British Standards Institution (2 Park St., London, W.1). B.S. 2540 : 1960. 12 pp.—Methods are given for the determination of moisture, pH, water-sol. chlorides and sulphates, and absorptive capacity.

N. E.

3183. **Determination of small amounts of germanium in ores and minerals.** K. G. Isaeva and L. G. Zhuravlev. *Trudy Inst. Mineral., Geokhim., i Kristallokhim. Redk. Element.*, 1959, (2), 278–284; *Ref. Zhur., Khim.*, 1960, (3), Abstr. No. 8867.—Sulphide ores are decomposed by fusion with Na_2O_2, and magnesium ores by boiling with HCl and H_2O_2; Ge is then distilled off as $GeCl_4$, which is determined photometrically with phenylfluorone. Iron ores are decomposed by HF, HNO_3 or H_3PO_4 and silicate ores by HF or H_2SO_4; $GeCl_4$ is then extracted by means of CCl_4. Topaz samples are decomposed by fusion with Na_2CO_3. Haematite - magnetite ores are chlorinated by heating with CCl_4 at 800° to 900° and $GeCl_4$ is then distilled from 6 *N* HCl.

K. R. C.

3184. **Photometric determination of tin.** T. N. Nazarchuk (Inst. of Gen. and Inorg. Chem., Acad. Sci., Ukr. SSR, Kiev). *Zhur. Anal. Khim.*, 1959, **14** (6), 696–699.—To determine Sn in metallic nickel dissolve the sample (1 g) in HCl and, if desired, 50% HNO_3, evaporate the soln. to 5 or 10 ml, add 5 or 6 ml of a saturated soln. of thiourea (to remove the interference of Fe) and neutralise with 4% NaOH soln. to a permanent cloudiness. Add a drop of *N* HCl, 1 ml of 10^{-3} *M* ethanolic quercetin, and an acetate buffer soln. (pH 4 to 5) to make 25 ml. Allow the soln. to stand for 5 min., transfer it to a separating-funnel, add 5 ml of a mixture of *iso*amyl alcohol and diethyl ether, shake carefully and allow the layers to separate. Remove the aq. layer and compare the colour of the organic layer with that of a series of standards prepared similarly. Less than 1 μg of Sn can be detected. No interference is caused by the presence of Hg, Ag, As, Al or Bi; < 20 μg of Sb in the sample does not interfere.

C. D. KOPKIN

3185. **Determination of small amounts of tin.** A. B. Russell (Defence Standards Lab., Maribyrnong, Victoria, Australia). *Analyst*, 1959, **84**, 712–716.—To prepare the calibration graph, aliquots of the standard soln. of metallic tin in HCl are treated with a specified amount of HCl, an aluminium pellet is added and the liquid is boiled. Each soln. is treated with a freshly prepared molybdosilicate reagent, and the extinction of the suitably diluted soln. is measured at 680 mμ. The sample is subjected to a wet-ashing procedure with HNO_3 and H_2SO_4; HNO_3 is finally removed by fuming and a suitable aliquot of the liquid is treated as described for the calibration. If the tin compound is an organotin compound and a suitable solvent is known, the compound may be extracted in a Soxhlet extractor, the extract being evaporated and the residue oxidised as before. The accuracy for 0·5 to 1·25 mg of Sn is within ± 2% and for 0·05 mg within ± 4%.

A. O. JONES

3186. **Polarographic determination of tin in the presence of interfering elements by using a bromide - chloride basal solution.** F. K. Baev. *Uch. Zap. Rostov. na Don Univ.*, 1958, **41**, 135–144; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,308.—The polarographic determination of Sn^{4+} with NH_4Cl -

HCl or NH_4Br - HCl as basal soln. has been investigated. The dependence of the diffusion current for Sn^{4+} on the time of leaving the soln. at different acidities has been studied. In dil. acid soln., as the result of the hydrolysis of Sn^{4+}, the diffusion current diminishes with time (*e.g.*, in 0·5 *N* HCl after 88 hr. the wave height is ≃ one-third; the same effect is observed in conc. acid soln. (3 *N* HCl). It is necessary therefore to use freshly prepared and conc. acid (5 to 6 *N* HCl) soln. The wave height is a linear function of the concn. of Sn when NH_4Cl - HCl is used as the basal soln. and remains approx. constant even for large changes in the ratio of NH_4Cl and HCl. There are two waves, separated by 0·28 to 0·3 V when NH_4Br - HCl is used as the basal soln.; the first is observed at − 0·08 V (relative to a mercury-pool anode). Because this first wave of the Sn^{4+} is clearly defined and observed at a more positive potential than the waves of a number of other metals, the determination of Sn in the presence of large amounts of Pb and Zn (up to 256 g per litre) is possible.

W. Roubo

3187. **Reactions of titanium(IV) in anhydrous media.** L. Sommer (Inst. for Anal. Chem., Brno Univ., Czechoslovakia). *Z. anal. Chem.*, 1959, **171** (6), 410–420 (in German).—The colours given by Ti^{IV} with more than 50 phenols and enols in conc. H_2SO_4, anhyd. methanol and dimethylformamide are listed. The colours in dimethylformamide are suggested as a means of detecting phenolic and enolic compounds. The reactions of Nb^{V}, Ta^{V}, Mo^{VI}, V^{V}, Sn^{IV} and Fe^{III} in conc. H_2SO_4 are also discussed.

H. M.

3188. **Spectrophotometric determination of titanium [in aluminium and its alloys] by the hydrogen peroxide method.** G. Matelli and L. Monti (Ist. Sper. Metalli Leggeri, Div. Ric., Novara, Italy). *Alluminio*, 1960, **28** (12), 553–557.—After dissolution of the sample (0·5 to 2 g) in H_2SO_4 - HNO_3 - HCl - H_2O (5:4:4:7), H_3PO_4 and H_2O_2 are added and the extinction of the soln. is measured at 400 mμ against a blank. In the presence of Bi, Sn, Pb, Cr and large amounts of Fe, Ni and Co, the interfering elements are removed electrolytically at a mercury cathode. Samples (10 g) with very low concn. of Ti are dissolved in 30% NaOH soln. and the residue is dissolved in acid and analysed for Ti; interfering elements are removed at a mercury cathode. For aluminium bronze, the sample (0·5 to 5 g) is dissolved in HNO_3 (1:4); in the presence of Sn, Sb, Bi, Pb and Ni, the interfering elements are removed at platinum electrodes. Small amounts of V do not interfere, but the method cannot be used if Mo and W are present. No interference is caused by a large excess of Al, Cu, Mg, Zn, Na, K, Ga, Ag, Be, B, Cd and Ce.

J. H. Waton

3189. **Determination of the sum of sesquioxides and titanium dioxide in apatite concentrate.** L. D. Nikitina ("Apatit" Combine). *Zavod. Lab.*, 1959, **25** (12), 1445–1446.—Partial dissolution of the sample (0·5 g) is carried out by heating it for 10 to 15 min. with 20 ml of HCl (1:1) and 10 ml of 5% boric acid soln. (to combine with F). After addition of 20 ml of 10% EDTA (disodium salt) soln. the soln. is neutralised to Congo red indicator with 25% aq. NH_3, and Al, Fe and Ti are pptd. by addition of 8 to 10 ml of a 3% soln. of 8-hydroxyquinoline in 5% acetic acid, 22·5 ml of ammonium acetate soln. [concn. not stated] and 6 ml of 25% aq. NH_3. The EDTA serves to retain in soln. Mn, alkaline-earth and rare-earth metals. The soln. is diluted to 150 ml and kept hot for 30 min. The ppt., including the insol. SiO_2, is collected, washed with 2% ammonium acetate soln., dried, ignited, and freed from SiO_2 by treatment with H_2SO_4 and HF. The residue is dissolved in 3 to 5 ml of water and 3 to 5 ml of HCl and the soln. is treated with 5 ml of 5% boric acid soln. and 3 to 5 ml of EDTA (disodium salt) soln., then neutralised to Congo red indicator, and treated with 10 to 12 ml of the 8-hydroxyquinoline soln., 15 ml of ammonium acetate soln. and 4 ml of aq. NH_3. The soln. is diluted to 100 ml and kept hot for 30 min., and the ppt. is collected, washed, ignited at ≃ 1000°, and weighed to give the content of sesquioxides and TiO_2.

G. S. Smith

3190. **Polarographic study of titanium and niobium in pyrophosphoric acid solutions.** D. I. Kurbatov (Inst. Chem., Ural Branch, Acad. Sci. USSR, Sverdlovsk). *Zhur. Anal. Khim.*, 1959, **14** (6), 743–744.—Titanium and Nb in pyrophosphoric acid soln. (sp. gr. 1·85) give clear reduction waves of $E_{\frac{1}{2}}$ 0·145 and 0·520 V, respectively, *vs.* the S.C.E., separately and when present together. The limiting currents are directly proportional to the concn.; this has been shown for soln. 0·9 to 25 m*M* in Nb and 4·65 to 17·25 m*M* in Ti, for ratios of Nb to Ti of up to 1:20.

C. D. Kopkin

3191. **Study of the polarographic behaviour of zirconium in acid medium and the presence of nitrate ions.** P. Mechelynck and C. Mechelynck-David (Centre d'Étude de l'Énergie Nucl. C.E.N., Mol, Belgium). *Anal. Chim. Acta*, 1959, **21** (5), 432–439 (in French).—Observed data for the polarography of 10^{-3} to 10^{-5} *M* Zr in acid soln. (pH 2 to 6) containing from 10^{-7} to 2×10^{-3} *M* NO_3^- are given and discussed. The reduction of NO_3^- at the dropping-mercury electrode is catalysed by Zr^{4+}, which accumulate at the electrode. The reduction wave for $ZrO_2^{2+} + 2H^+ = Zr^{4+} + H_2O$ can be used for the determination of NO_3^- in concn. of 10^{-5} to 5×10^{-3} *M* at pH 2, provided that the concn. of ZrO_2^{2+} is ≃ 10^{-3} *M*.

W. J. Baker

3192. **Separation of zirconium from titanium, ferric iron, aluminium and other cations by cation-exchange chromatography.** F. W. E. Strelow (Nat. Chem. Res. Lab., S. Afr. Council Sci. Ind. Res., Pretoria). *Anal. Chem.*, 1959, **31** (12), 1974–1977.—Zirconium (≡ > 200 mg of ZrO_2) can be completely separated from Ti, Fe^{3+} and Al by adsorption of the four elements (in acid soln.) on to a column (22 cm × 1·15 cm) of AG50 WX8 resin (100 to 200 mesh), followed by elution of Ti, Fe^{3+} and Al with 2*N* HCl (300 to 400 ml) and then of Zr with 5*N* HCl (400 ml) at rates of flow from 2 to 4 ml per min. The Zr in the eluate can be determined as pyrophosphate; the results agree well with those obtained by direct gravimetry, *e.g.*, 0·207% against 0·202% of ZrO_2 for a flint clay. Other cations that are completely eluted with 2 *N* HCl are Cu^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Sn^{2+}, Sn^{4+}, UO_2^{2+}, Be^{2+}, Mg^{2+}, NH_4^+, Li^+, Na^+, K^+ and Rb^+; the method can be modified so as to separate Ca, Ba, Sr, Th, Cr^{3+} and tervalent rare-earth elements from Zr. Oxalate and F^- should be absent from the soln. and SO_4^{2-} in concn. > ≃ 0·1 *N* should preferably be removed. The procedure is specially suitable for the separation of 1 to 10 mg of Zr from other elements.

W. J. Baker

3193. **Absorptiometric determination of molybdenum and tungsten in zirconium metal.** U.K.A.E.A. Production Group (Chemical Services Dept., Springfields, Lancs.). U.K.A.E.A. Rep. PGR-25(S), 1959. 7 pp.—Molybdenum and W are determined absorptiometrically as the dithiol complexes, after extraction from an aq. soln. of the metal at controlled acidity. The analysis is applicable to samples of zirconium metal and sponge. NUCL. SCI. ABSTR.

3194. **Determination of traces of rare-earth [metals] in zirconium and its alloys.** D. F. Wood and M. Turner (Res. Dept., I.C.I. Ltd., Metals Div., Kynoch Works, Witton, Birmingham, England). *Analyst*, 1959, **84**, 725–731.—The sample is dissolved in HF and HNO_3, yttrium oxide dissolved in HCl is added as a carrier, and ytterbium oxide dissolved in HCl as a control on the degree of recovery of other rare-earth metals. The rare-earth metals are pptd. as fluorides, the ppt. is collected, ignited, evaporated to dryness with H_2SO_4, dissolved in HCl and pptd. as oxalate, which is collected and ignited. The rare-earth metals in the residue are then determined spectrographically by comparison with standard spectra. The limits of detection for specified rare-earth metals ranged from 0·02 p.p.m. to 0·5 p.p.m.

A. O. JONES

3195. **Method for concentrating thorium from nitric acid - ethanol solution with Dowex-1 strongly basic anion - exchange resin. Its use in the determination of thorium in silicate rocks.** J. Korkisch and P. Antal (II Chem. Univ. Lab., Vienna, Austria). *Z. anal. Chem.*, 1959, **171** (1), 22–27.—The sample (1 g) is attacked twice with conc. HNO_3 - HF (1 : 1) and, after evaporation, the residue is treated with 5 ml of conc. HNO_3 and again evaporated to remove F^-. The dry residue is dissolved in 25 to 30 ml of 3·5 *N* HNO_3, warmed gently, then filtered into a 100-ml flask and the filter is washed with 3·5 *N* HNO_3. To 25 ml of this soln. is added 100 ml of ethanol and after 1 to 2 hr. the soln. is passed through a column of Dowex 1 (nitrate form) at a rate of 0·5 ml per min. Thorium is then eluted from the column with 100 ml of 0·1 *N* HNO_3 satd. with diethyl ether and determined photometrically at 545 mμ with thoron by the method of Banks and Byrd (*cf. Brit. Abstr. C*, 1953, 296). Results for added Th (10 μg) in silicate rocks show deviations up to 10% of the theoretical.

B. B. BAUMINGER

3196. **Gravimetric determination of thorium and cerium with N-benzoyl[-N-]phenylhydroxylamine.** S. K. Sinha and S. C. Shome (Presidency Coll., Calcutta, India). *Anal. Chim. Acta*, 1959, **21** (5), 415–417.—Milligram amounts of Th and Ce^{3+} can be quant. pptd. at 25° by N-benzoyl-N-phenylhydroxylamine (0·3 to 0·4 g in 12 ml of ethanol) at pH 4·5 to 5·5 (for Th) or pH 6·5 to 7 (for Ce^{3+}). The ppt. can be ignited to the dioxide and weighed. A soln. containing Ce^{4+} should be initially reduced with hydroxyammonium chloride. The error is −0·0005 g for ≃ 0·08 g of Th and ± 0·0004 g for ≃ 0·06 g of Ce. When present together the two elements can be separated and determined by successive pptn. at the two different values of pH.

W. J. BAKER

3197. **Photometric determination of thorium in zircon by means of the new reagent Arsenazo III.** V. F. Luk'yanov, S. B. Savvin and I. V. Nikol'skaya. *Zavod. Lab.*, 1959, **25** (10), 1155–1157.—A soln. of Arsenazo III [2 : 7-di-(*o*-arsonophenylazo)-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid] (**I**) gives a green or blue - violet colour with small amounts of Th and a ppt. with large amounts. The complex forms even in 6 *N* HCl. Similar colours are given by Zr, Hf and U^{IV}. With contents of Th from 1 to 35 μg in 50 ml the colour obtained is stable for 1·5 hr. In the presence of Zr and Ti, oxalic acid is added to form stable complexes. The sample (100 mg) is fused with 0·5 g of anhyd. KHF_2 at 800° to 900°. The melt is heated first with 10 ml, and then with a further 5 ml, of dil. H_2SO_4 (1 : 1), and the soln. is evaporated to remove HF and ignited to remove SO_3. The residue is dissolved in 25 ml of 6 *N* HCl and diluted to 50 ml, and an aliquot is diluted with 3 *N* HCl to 20 ml. If the soln. is yellow (Fe^{III}) a few crystals of ascorbic acid are added. The soln. is then treated with 6 ml of 6 *N* HCl, 20 ml of 4% oxalic acid soln. and 2 ml of reagent soln. (prepared by dissolving 0·1 g of **I** in water, adding 5 ml of 6 *N* HCl, and diluting to 100 ml). The extinction of the soln. is measured after dilution with 6 *N* HCl to 50 ml. The method is applicable to contents of Th ≮ 0·005%.

G. S. SMITH

3198. **Polarographic determination of hydroxylamine alone and in comparison with hydroxamic acid(s).** T. Østerud and M. Prytz (Univ. Farm. Inst., Blindern-Oslo, Norway). *Acta Chem. Scand.*, 1959, **13** (10), 2114–2118 (in English).—Polarograms of hydroxylamine (**I**), and aceto- and propronohydroxamic acids are recorded in ethanol - water soln., with tetraethylammonium iodide as base electrolyte, and tetraethylammonium hydroxide for adjusting the pH. Without addition of the alkali the pH of the system is 5·4 and **I** gives three waves at $E_{\frac{1}{2}} = -1{\cdot}44$, $-2{\cdot}1$ and $-2{\cdot}35$ V *vs.* the S.C.E.; as the pH is raised the first wave disappears at pH 5·6, the second wave decreases in height from pH 11, and the third remains constant at a low height. Above pH 14 the second wave coalesces with the third. The waves due to **I** decrease and finally disappear when the alkaline soln. is allowed to stand, and this effect is accelerated by heating. The hydroxamic acids give waves at 0·1 V higher and 0·2 V lower than the corresponding waves due to **I** and are not destroyed by heating. It is shown that the hydroxamic acids may be determined even in the presence of an excess of **I** by polarography at pH 11·7 to 12·3, after heating for a short time on a water bath and cooling to room temp.

E. J. H. BIRCH

3199. **The separation of hyponitrite from nitrite, nitrate and hydroxylamine by paper chromatography.** H. M. Stevens (Long Ashton Res. Station, Bristol, England). *Anal. Chim. Acta*, 1959, **21** (5), 456–459.—The preparation of CO_3^{2-}-free sodium hyponitrite by a modification of the process of Addison *et al.* (*J. Chem. Soc.*, 1952, 338) is described. A mixture of $Na_2N_2O_2$, $NaNO_2$, $NaNO_3$ and hydroxyammonium sulphate can be resolved by downward chromatography of the soln. (in 2 *N* NaOH) on strips of Whatman No. 1 paper in a developing soln. containing ethanol (70 ml), water (30 ml) and NaOH (2 g). The upper (NaOH) zone of the chromatogram contains $N_2O_2^{2-}$ (R_F 0·1), whilst the lower (ethanol - H_2O) zone contains NO_2^-, NO_3^- and hydroxylamine (R_F 0·5 to 0·6). The procedure is useful for checking the purity of, *e.g.*, $Ag_2N_2O_2$ pptd. with $AgNO_3$. The spots of $N_2O_2^{2-}$ and NO_3^- are developed with resorcinol - sodium periodate (*Analyst*, 1959, **84**, 119), followed by exposure to u.v. light of the brown spots so obtained. The orange fluorescence

of 1 μg of $N_2O_2^{2-}$ is easily detected, and 1 μg of NO_2^- can be seen even in daylight. An unidentified impurity was present in trace amounts in the prepared $Na_2N_2O_2$. W. J. BAKER

3200. **Application of metal-specific indicators to precipitation titrations. V. The exact rapid determination of small quantities of orthophosphate in the presence of sulphate.** E. Lassner, R. Püschel and R. Scharf (Chem. Lab. d. Versuchsanst. d. Metallwerk Plansee A.-G., Reutte, Tirol). *Z. anal. Chem.*, 1959, **170** (2), 412–419 (in German).—Phosphate is rapidly and quant. pptd. by titrating with a standard soln. of Ce^{III}, with Eriochrome black T as indicator. In the absence of SO_4^{2-}, the titration can be carried out with standard $Pb(NO_3)_2$ soln., with 4-(2-pyridylazo)resorcinol as indicator. *Procedure*—Neutralise the sample soln. to methyl red and heat to boiling. Add indicator buffer powder (hexamine, Zn - EDTA complex and Eriochrome black T, 4000 : 3 : 1) until a clear blue colour is obtained, then 0·5 to 1 g of hexamine, and titrate with 0·05 or 0·005 *M* Ce^{III} soln. to a red end-point. Chloride, NO_3^-, SO_4^{2-}, molybdate, tartrate, acetate and borate do not interfere, but citrate, fluoride, silicate, arsenate, antimonate, vanadate, tungstate and metals that react with Eriochrome black T do. For quantities of PO_4^{3-} between 0·3 and 30 mg the precision is $\simeq$ 1%. W. T. CARTER

3201. **Colorimetric determination of impurities in arsenic.** L. B. Kristaleva (V. V. Kuĭbyshev Tomsk State Univ.). *Zavod. Lab.*, 1959, **25** (11), 1294–1295.—The determination of Sb is carried out photometrically by means of the reaction of $SbCl_6^-$ in HCl soln. with Brilliant green. The complex gives a bluish-green colour in benzene, toluene or xylene, and the reagent is not extracted. Beer's law is obeyed over the concn. range of 1 to 5 μg per ml and the colour is stable for 24 hr. No interference is caused by As, Cu, Ni, Zn, Co or Pb if the amount present is $\not>$ 1000 times that of the Sb. Greenish colours are given by Sn, Hg, Cd and Fe, but these are stable for $\not>$ 10 to 15 min. The interference of Fe can be prevented by the addition of NaF. Diethyldithiocarbamate is used for determining Cu. G. S. SMITH

3202. **Determination of copper and iron impurities in arsenic by ion exchange.** L. N. Rozanova and G. A. Kamaev (Tomsk State Univ., USSR). *Zhur. Prikl. Khim.*, 1959, **32** (11), 2574–2575.—*Procedure*—Dissolve the arsenic (2 to 5 g) by heating in conc. HNO_3 (sp. gr. 1·4), evaporate the soln., add HCl to dissolve the residue, evaporate the soln. to the smallest possible vol. and adjust the pH of the soln. to 1·5. Pass the soln. through a cationite (1-cm mesh, in a layer 6 to 7 cm in height) (H^+ form), wash the column with H_2O (50 ml) to remove the remaining acid, and elute the adsorbed impurities first with *M* Na K tartrate (12·5 ml) to which 2 *M* aq. NH_3 (1 ml) has been added, then with 2 *M* aq. NH_3 (6 ml) and finally with H_2O. Dilute the combined eluates to 25 ml and polarograph with a supporting electrolyte of 0·5 *M* Na K tartrate and 0·5 *M* aq. NH_3, and an S.C.E. After recording the two copper waves (−0·2 to 0·8 V), using the second one for the calculation, add 0·5% gelatin soln. (5 drops per 25 ml of soln.) and determine Fe^{3+}; the heights of the waves are directly proportional to the concn. Calculations are made with reference to a calibration curve. K. R. C.

3203. **Determination of antimony and arsenic in [copper electrolytic] slimes.** A. N. Polukarov and O. K. Selyanina (Pyshminsk Electrolytic Copper Works). *Zavod. Lab.*, 1959, **25** (12), 1447–1448.—The sample (0·5 to 1 g) of slime is mixed with 100 mg of tin foil or filings (to ensure that Sb remains completely with the matter insoluble in HNO_3) and boiled for 6 to 10 min. with 25 to 30 ml of HNO_3. The soln. (10 to 15 ml) is diluted to between 70 and 80 ml, boiled, cooled somewhat, and filtered. The filtrate is analysed for As by the distillation method, including titration with $KBrO_3$ soln. The insol. matter is heated with H_2SO_4 in the presence of the filter-paper, and the clear colourless soln. is diluted, reduced with SO_2, and titrated with $KBrO_3$ soln. G. S. SMITH

3204. **Separation of antimony(V) from iron(III), copper(II), cobalt(II) and cadmium(II) by ion exchange.** S. S. M. A. Khorasani and M. H. Khundkar (Univ., Dacca, East Pakistan). *Anal. Chim. Acta*, 1959, **21** (5), 406–410.—The separation is effected by passing the sample soln., containing an excess of aq. 20% tartaric acid, through a column of Zeo-Karb 225 (H^+ form) at the rate of 30 to 40 drops per min. The ions Cu^{2+}, Fe^{3+}, Co^{2+} and Cd^{2+} are quant. retained on the column, whilst the percolate contains the stable anionic complex of Sb^{5+} and can be analysed for Sb by the iodimetric method. The error is $\pm$ 1%. The method is inapplicable when Hg^{2+}, Sn^{3+} or Sn^{4+} are present because these ions are not adsorbed on the resin. W. J. BAKER

3205. **Concentration by sublimation in the determination of small amounts of impurities in antimony.** A. S. Andreev. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 35–39; *Ref. Zhur., Khim.*, 1960, (3), Abstr. No. 8957.—When finely divided antimony metal is heated with a 4-fold amount of NH_4Cl at 380° to 400°, a mixture of $SbCl_3$ and NH_4Cl sublines; metal chlorides formed as a result of the decomposition of NH_4Cl into NH_3 and HCl are not removed (Pb, Mn and Na are completely retained and the loss of Ni, Co, Fe and Cu is insignificant). This sublimation facilitates the subsequent determination of impurities, especially of Na, which is not quant. removed by the usual method of dissolution of the sample in HCl (neither Na_3Sb nor NaSb is dissolved). A modified zinc uranyl acetate method is described for the determination of Na after sublimation of Sb with NH_4Cl. K. R. C.

3206. **Gravimetric and titrimetric determination of bismuth with the ammonium salts of benzene- and naphthalene-selenic acids.** V. S. Sotnikov and I. P. Alimarin (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1959, **14** (6), 710–713.—Bismuth can be determined in the presence of Ag, Be, Ca, Al, Zn, Mn, Ni, Co, Cd, Cu and Pb by pptn. with the reagents named, which precipitate Bi from mineral acid soln. as $(RSeO_3)_3Bi$, a white crystalline ppt. soluble in conc. acid and decomposed by alkali. The ppt. is filtered off, washed with water, dried at 110° to 120° and weighed; for titration, the ppt. is filtered off, washed, and transferred to a titration vessel; a little HCl is added, followed by 0·5 to 1·0 g of tartaric acid, and the soln. is heated to dissolve the ppt. The mixture is then diluted, a 2- or 3-fold excess of KI is added, and the liberated iodine is titrated potentiometrically or amperometrically with $Na_2S_2O_3$ soln. After the pptn. of Bi, Pb can be determined in the filtrate by

pptn. with thiourea, followed by conversion into $PbCrO_4$, and finally iodimetric titration. Up to 10% of Pb does not interfere in the determination of Bi, but with > 10% of Pb the Bi should be re-pptd. The relative error (5 to 20 mg of Bi) is ≯ 0·5%.
C. D. KOPKIN

3207. **Determination of vanadium by photometric titration.** H. Hartkamp (Inst. für Spektrochemie u. angew. Spektroskopie, Dortmund-Aplerbeck). *Z. anal. Chem.*, 1959, **171** (4), 262–270 (in German).—The determination of V^V with H_2O_2 is dependent on pH and H_2O_2 concn. By chelating the resulting peroxy compound with pyridine-2:6-dicarboxylic acid (**I**), a more stable system is obtained. A 4-fold excess of Nb, Ta, Th, Sn, Zr, Sb or Cu interferes; only traces of Ti should be present. Common anions do not interfere. *Procedure for vanadium in steel*—Dissolve the sample (0·3 to 2 mg of V) in 15 ml of HCl - HNO_3 (3:1), dilute to 40 ml, filter, and wash the residue. To the filtrate in a titration cell add 0·5 to 2 ml of 30% H_2O_2 and a little H_3PO_4, mix and adjust the photometer reading to zero. Titrate with aq. 0·02 *M* **I** and measure the extinction at 432 mμ, extrapolating to obtain the end-point. Beer's law is followed when ≯ 120 μg of V per ml is present.
P. D. PARR-RICHARD

3208. **Colorimetric method for determination of vanadium employing 1-(2-pyridylazo)-2-naphthol.** F. W. Staten and E. W. D. Huffman (Huffman Micro-anal. Lab., Wheatridge, Colo., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2003–2007.—The procedure applies to the routine determination of V (0·03 to 50%) in either ferrous alloys or ores and refractories. After dissolution of the sample, removal of interfering elements by pptn. as hydroxides, and further treatment of the soln. (containing 20 to 50 μg of V and adjusted finally to pH 3·5), the coloured complex of VO_2^+ with 1-(2-pyridylazo)-2-naphthol is formed at ≃ 25° (at least 4 hr. should be allowed for colour development). The complex is then extracted into $CHCl_3$ and its extinction is measured at 615 mμ in a 1-cm cell, with $CHCl_3$ as a reference. Residual Fe is corrected for or compensated spectrophotometrically; Beer's law is followed in the range of 9 to 61 μg of V in 25 ml of $CHCl_3$. The sensitivity varies with pH, which should be reproduced within ± 0·1 unit for sample soln. and standards; a pH of 4·5 is preferred for high contents of V. Interference by anions and other substances is discussed.
W. J. BAKER

3209. **Colorimetric determination of vanadium in titanium tetrachloride.** F. G. Zharovskiĭ and A. T. Pilipenko. *Ukr. Khim. Zhur.*, 1959, **25** (2), 230–236; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,313.—The extraction of the V - N-benzoyl-N-phenylhydroxylamine (**I**) complex by $CHCl_3$ and the optical properties of the $CHCl_3$ extracts of the complexes of V, Ti and Fe with **I** have been studied. It has been established that in the vanadium complex the molar ratio of V to **I** is 1:2, and it has been suggested that the composition of the complex corresponds to $V_2O_3(C_{12}H_{10}O_2N)_4$. A photometric method for the determination of V in titanium tetrachloride, based on the extraction with $CHCl_3$ of the V - **I** complex, has been evolved. Additions of NaF and H_3PO_4 are made to remove the interference of Ti and Fe, respectively. The complete determination takes 10 to 15 min.; the determinable concentration of V is 0·01 to 0·3%.
W. ROUBO

3210. **Spectrochemical determination of niobium in rocks.** N. I. Tarasevich and K. A. Semenenko (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1959, **14** (6), 705–709.—*Procedure*—Decompose the sample (≃ 1 g) with a mixture of HF and H_2SO_4 till all SiO_2 has been removed. Dissolve the residue in dil. HCl, heat, and to the soln. (pH 1) add silica gel, gelatin soln., pyrogallol and paper pulp. Set the mixture aside on a water bath for 2 to 3 hr. and filter after leaving it overnight. Ignite the ppt., and determine Nb spectrographically. The ignited ppt. will contain Ta, Ti, Fe and Al in amounts which do not interfere in the determination of Nb. This procedure has been tested on artificial mixtures similar to granites. The completeness of the pptn. of Nb on silica gel was shown radiochemically. As little as 10^{-5} % of Nb in gneiss and granite can be determined with an error of ≃ 20%.
C. D. KOPKIN

3211. **Separation of niobium and tantalum by the liquid extraction method.** D. I. Ryabchikov and M. P. Volȳnets (V. I. Vernadskiĭ Inst. Geochem. and Anal. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (6), 700–704.—By using the radioactive isotopes ^{95}Nb and ^{182}Ta, it has been shown (*i*) that 90% of the Ta is extracted from *M* HF with tributyl phosphate, while Nb remains almost completely in the aq. phase; (*ii*) that the presence of HCl or H_2SO_4 increases the extraction of Nb; (*iii*) that the tributyl phosphate can be diluted with 20% (v/v) of hydrogenated kerosine (boiling-range 200° to 230°) without much affecting the extraction of Ta, this dilution facilitating the separation of the layers; and (*iv*) that increase of temp. decreases the extraction of Ta. To analyse tantalum - niobium alloys, ignite at 800° to 900°, fuse a sample of the pentoxides (500 mg) with $K_2S_2O_7$, extract the melt with conc. H_2SO_4, dilute the extract, precipitate the hydroxides and dissolve them in *M* HF. Extract (× 2) at 20° with equal volumes of a mixture of tributyl phosphate and kerosine (4:1) satd. with *M* HF, and determine Nb in the aq. phase and Ta in the organic phase (after re-extraction with a 4% soln. of ammonium oxalate and boric acid) by pptn. with phenylarsonic acid or aq. NH_3, after evaporation of the soln. with H_2SO_4 and dilution. Ignite the ppt. to pentoxides and weigh. The results for Ta are somewhat high owing to partial extraction of Nb (≃ 2 to 3%) by tributyl phosphate. A single extraction in a counter-current continuous-action sectionally-packed column (described) can produce Nb of 99·7 to 100% purity; the Ta contains > 1% of Nb.
C. D. KOPKIN

3212. **Determination of niobium in uranium - niobium alloys.** G. W. Goward, T. M. Reinhold and V. R. Wiederkehr (Westinghouse Electric Corp. Bettis Plant, Pittsburgh). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-543, Feb., 1958. Decl. Nov., 1959. 4 pp.—The alloy is dissolved in HF and HNO_3 and the fluoride is removed by fuming with H_2SO_4. The niobium is hydrolysed in an acid - SO_3 medium and converted to niobic oxide by ignition at 900°. The method covers the determination of niobium in niobium - uranium alloys having a niobium content of 8 to 12%. Metals which hydrolyse readily in dilute acid soln. interfere with the determination.
NUCL. SCI. ABSTR.

3213. **Volumetric determination of carbon disulphide as diethyldithiocarbamate.** V. Šedivec and J. Flek (Inst. Works Hyg. and Occup. Diseases,

Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3643–3648 (in German).—The method is based on the reaction of CS_2 with diethylamine and titration of the diethyldithiocarbamate so produced with $HgCl_2$ soln. *Procedure*—Into a 100-ml flask place diethylamine soln. (6 ml of 33% aq. soln., diluted to 100 ml with pyridine) (5 ml), dilute with pyridine to 25 ml and add the soln. of the sample (0·5 to 15 mg of CS_2 in 5 to 25 ml). Mix, add the indicator soln. [a mixture of 0·1 *M* $CuSO_4$ with a small excess of 0·1 *M* EDTA (disodium salt)] (1 drop) and titrate with 0·01 *N* $HgCl_2$ till the yellow or brown colour is discharged. Methanol, ethanol, acetone, benzene, toluene, xylene, hexane and petrol do not interfere. When analysing coloured samples, CS_2 must be separated by distillation. The removal of interfering substances (*e.g.*, thiols) is discussed.

J. ZÝKA

3214. **Determination of inorganic polysulphides.** E. Bilberg and P. Landmark. *Norsk Skogindustri*, 1959, **13** (11), 375–382 (in English).—Two methods for the determination of polysulphides in black liquor were investigated and compared with that of Kurtenacker and Bittner (*Z. anorg. Chem.*, 1925, **142**, 115) by analysing synthetic soln. of polysulphides prepared by dissolving elementary sulphur in sulphide soln. One method is based on the reaction of polysulphide with metallic copper, the copper sulphide formed being separated and determined iodimetrically. The other method is based on the same principle as that of Kurtenacker and Bittner, *viz*, the determination of the increase in thiosulphate following an addition of excess of sulphite to the polysulphide-containing soln., but differs from the latter method in that the thiosulphate is titrated with $HgCl_2$ soln. instead of being determined iodimetrically. The copper method gave reproducible results which agreed well with the amounts of sulphur added, whereas the other methods gave somewhat lower and less reproducible results. The copper method is suitable for determining relatively small amounts of polysulphide (down to 0·02 g per litre), particularly if the soln. is protected against oxidation (by flushing with pure N or by covering with a paraffin layer) during the reaction with Cu. Rotating the copper gauze produces a more adherent copper sulphide layer, gives more reproducible results and decreases the reaction time necessary. For most practical purposes, however, the differences between the three methods are of minor importance, and all three should be applicable.

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3215. **Photometric determination of micro amounts of sulphides and sulphur in metals by catalysis of the iodine - azide reaction.** A. K. Babko and L. V. Markova (Inst. of Gen. and Inorg. Chem., Acad. Sci., UkrSSR). *Zavod. Lab.*, 1959, **25** (11), 1283–1287.—The optimum conditions for catalysis of the iodine - NaN_3 reaction by S^{2-} are studied. Concn. of reagents applicable to four concn. levels of S^{2-} within the range 0·01 to 60 μg per 10 ml are recommended. Samples of steel are decomposed with dil. HCl (3:1) and the H_2S evolved is absorbed in NaOH soln.

G. S. SMITH

3216. **Rapid method for the volumetric determination of sulphates in waters, soil extracts and biological material.** A. Badrinas (Inst. de Biol. Aplicada, Lab. de Fisiol. Vegetal, Univ. de Barcelona, Spain). *Inf. Quim. Anal.*, 1959, **13** (6), 178–180.—The soln. containing SO_4^{2-} is treated with 0·02 *N* Pb acetate and the excess of this reagent is determined by titration with EDTA (disodium salt) soln., with dithizone as indicator. The method is useful for soln. containing small amounts of SO_4^{2-} (up to 0·3%) and is accurate to within $\pm$ 0·5%. Citrates, tartrates, oxalates, PO_4^{3-}, Cl^-, Br^- and I^- interfere.

G. H. FOXLEY

3217. **Colorimetric method for the rapid determination of traces of selenium.** E. M. Ray (Goodyear Atomic Corp., Portsmouth, Ohio). *U.S. Atomic Energy Comm.*, Rep. GAT-289, Dec., 1959. 11 pp.—The colorimetric determination of Se in 5 to 50-mg amounts is described. Reduction of Se^{IV} and Se^{VI} to Se in aq. soln. is effected by HCl and HI, respectively, and the Se forms a coloured complex with the liberated iodine. Excess of iodine produced in side reactions combines with phenol. Results may be duplicated with a precision of $\pm$ 10%. The effects of oxidants, reductants, precipitants and other sources of interference were studied. Of those investigated, only Te causes serious difficulty.

NUCL. SCI. ABSTR.

3218. **Determination of tellurium in lead - antimony - tellurium alloys.** I. P. Onufrienok and V. M. Aksenenko (Tomsk Polytech. Inst.). *Zhur. Anal. Khim.*, 1959, **14** (5), 637–638.—Heat the sample, containing 1 to 20 mg of Te, for 10 min. with 2 ml of HNO_3 (sp. gr. 1·4) and 3 ml of 30% tartaric acid per gram of sample. Add 10 to 20 ml of water and boil to remove oxides of N, and neutralise the hot soln. with 40% NaOH soln.; stop the addition of NaOH soln. when the small flakes of undissolved $Pb(OH)_2$ begin to change into a heavy cryst. ppt. of Pb tartrate. To the almost boiling soln. add dropwise and with stirring 20% $SnCl_2$ soln. till Te (and Se, Ag, Au and Cu) is completely reduced. After 5 or 10 min. wash the tellurium ppt. in the flask 3 or 4 times by decantation with small portions of hot 30% ammonium acetate soln. to remove Pb, and then 3 or 4 times with hot 2% Na_2SO_4 soln., transferring the ppt. to the filter. Place on the filter 0·1 to 0·2 g of $NaNO_3$, cover the funnel with a watch-glass, and rapidly introduce under the latter 2 or 3 ml of a mixture of 2 ml of HNO_3 (sp. gr. 1·4) and 3 ml of 30% tartaric acid. When the Te has dissolved wash the filter-pad with 1% HNO_3. Boil the filtrate for 2 to 3 min., neutralise to phenolphthalein with 40% NaOH soln. and add 6 drops in excess, heat and, if metallic Ag separates, filter through a pad of glass wool and asbestos and wash the filter with hot 2% Na_2SO_4 soln. To the filtrate add, depending on the copper content, from 1 to 10 ml of 2 *N* $K_4Fe(CN)_6$ and 5 ml of a freshly prepared 20% soln. of lactose and boil for 15 or 20 min. till the ppt. of Te has coagulated. Filter on a pad of glass wool and asbestos and wash the ppt. by decantation and on the filter with hot 2% Na_2SO_4 soln. Wash the ppt. and asbestos back into the flask with water. Wash the funnel and the glass wool with < 10 ml of 4 *N* H_2SO_4 and slowly add 15 ml of 0·1 *N* $K_2Cr_2O_7$ to dissolve any remaining particles of Te. Wash the funnel with the remainder of the 10 ml of 4 *N* H_2SO_4 and with water. Warm the filtrate to 50° or 60°. Cool, reduce the excess of $K_2Cr_2O_7$ with 0·1 *N* H_2O_2, added slowly till the soln. is pure green, add a little in excess, and immediately titrate the excess of H_2O_2 with 0·1 *N* $KMnO_4$ to a sharp colour change from green to lilac. The content (%) of Te in the alloy is calculated from the formula—$[(v_1N_1 + v_2N_2) - v_3N_3] \times 2{\cdot}127/w$,

where v_1, v_2 and v_3 and N_1, N_2 and N_3 are the volumes and normalities of the soln. of $K_2Cr_2O_7$, $KMnO_4$ and H_2O_2, and w is the wt. of sample. The determination of Te in a sample and a control takes 2 to 3 hr. With a content of Te of 1 to 20 mg the relative error varies from 1 to 3%.

C. D. KOPKIN

3219. **Determination of small amounts of chromium in minerals and rocks with *sym.*-diphenylcarbazide.** F. Fröhlich (Mineralogisch-petrographischen Inst., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1959, **170** (2), 383–387 (in German).—After fusion of the sample with Na_2O_2 in a corundum crucible the melt is dissolved in water and heated on a water bath for 2 hr. to destroy H_2O_2. Iron is removed by passage through a cation-exchange column and the Cr is then determined colorimetrically as the *sym.*-diphenylcarbazide complex at 540 mμ. Vanadium in concn. up to 10 times that of the Cr can be tolerated if the soln. is set aside for 15 min. after colour development to allow the colour due to the V - diphenylcarbazide complex to fade. At the 100-μg level the relative error is ± 2%.

W. T. CARTER

3220. **Polarographic determination of chromium in aluminium alloys.** M. Ariel and G. Selzer (Israel Inst. Technol., Haifa). *Anal. Chim. Acta*, 1959, **21** (5), 425–429.—The sample (containing ≃ 1 mg of Cr) is dissolved in a boiling mixture of bromine water and conc. NaOH soln.; after suitable treatment the soln. is filtered (to remove hydroxides of Fe, Cu, Mn, Ni and Pb), and Cr^{6+} in the filtrate are then determined polarographically in 3% NaOH soln. at strictly const. temp. The accuracy is high provided that the diffusion current of the blank is deducted from that of the sample soln. The polarograms are recorded from −0·3 V to −1·3 V *vs.* the S.C.E., and the diffusion currents at $E_{\frac{1}{2}} = -0{\cdot}85$ V are calculated as described. The procedure is applicable to alloys containing 0·1 to 0·5% of Cr. The Zn, Al and Ti in the filtrate do not interfere.

W. J. BAKER

3221. **Determination of chromium in metallic nickel by extraction of the *sym.*-diphenylcarbazide complex.** A. K. Babko and T. E. Get'man (Inst. of Gen. and Inorg. Chem., Acad. Sci., UkrSSR). *Zavod. Lab.*, 1959, **25** (12), 1429–1430.—Extraction of the *sym.*-diphenylcarbazide complex by means of *iso*amyl alcohol serves to separate Cr from Co, Al, Ti and Mn, and also from Fe if EDTA is present. Prior removal of Cu as the dithizonate or as the metal pptd. by zinc amalgam is necessary. The sample (0·5 g) of metallic nickel is dissolved in 5 ml of HNO_3 (1:1) and 5 ml of H_2SO_4 (1:1) and the boiled and then cooled soln. is treated with zinc amalgam, diluted to 50 ml and then filtered. An aliquot (10 ml) is boiled for 5 to 7 min. with 0·5 ml of 0·1 *N* $AgNO_3$ and 5 ml of 20% $(NH_4)_2S_2O_8$ soln., cooled, treated with 2 ml of H_3PO_4 (1:2) to combine with Fe and 5 ml of 10% NaCl soln. to combine with any Hg that has dissolved, well shaken, then treated with 2 ml of a 1% soln. of *sym.*-diphenylcarbazide in acetone, shaken again, and after 1 min. treated with 10 ml of 0·1 *M* EDTA (disodium salt). To avoid reduction of CrO_4^{2-}, the EDTA must be added after the *sym.*-diphenylcarbazide. The soln. is then shaken with 15 ml of *iso*amyl alcohol and 15 g of solid NaCl, and the separated aq. layer is shaken with 5 ml of *iso*amyl alcohol. The combined extracts are diluted to 25 ml with *iso*amyl alcohol, and the extinction of the filtered soln. is measured at 540 mμ. Satisfactory results were obtained with contents of Cr in the range 0·0016 to 0·0100%.

G. S. SMITH

3222. **Determination of oxygen in high-purity chromium.** N. V. Ageev, A. I. Ponomarev and V. A. Trapeznikov. *Zhur. Prikl. Khim.*, 1959, **32** (11), 2479–2487.—The chemical method is simpler and more reliable than the vacuum-fusion method for the determination of all forms of oxygen ("free" or chemically combined) in chromium metal. *Procedure*—Calcine the sample (2 to 5 g when the oxygen content is less than 0·005%) in a sealed quartz ampoule (evacuated at room temp. to ≃ 10^{-4} torr) at 805° to 900° for 2 hr., cool to room temp., and unseal it. Add 10% HCl (100 to 200 ml) to the residue and heat on a sand bath until it is completely dissolved; stir the soln. periodically and make up to vol. when necessary. Cool the soln. and set it aside for not less than 2 hr. to ensure coagulation of the sub-microscopic Cr_2O_3 particles. Filter the soln. and wash the insol. Cr_2O_3 on the filter with cold 4 to 5% HCl. Finally wash the ppt. on the filter with H_2O, dry the ppt. and the filter-paper in air, incinerate the filter-paper and calcine the residue to a const. wt. at 800° to 900° for 1·5 hr. Then oxygen (%) = wt. of Cr_2O_3 × 0·3157/wt. of metal × 100. The accuracy of the method is ± 10%; the determinable minimum is 0·001% by wt. under the conditions described. The determination of oxygen in industrial chromium is not so accurate since several corrections have to be made for combined oxygen in Al_2O_3 and SiO_2 and also for carbides which require special methods of analysis.

K. R. C.

3223. **Use of metal reductors and amalgams in chemical analysis. II. The redox behaviour of molybdenum.** J. Doležal, B. Moldan and J. Zýka (Dept. of Anal. Chem., Charles' Univ., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3769–3776 (in German).—The reduction of Mo^{V} with zinc amalgam and the oxidimetric titration of the Mo^{III} was studied. It is stated that only in an acid medium containing a sufficient amount of Cl^- is a red complex of Mo^{III} formed that can be reliably titrated potentiometrically with oxidising agents. *Procedure for Mo and Fe in ferromolybdenum*—Dissolve the finely powdered sample (1 g), with gentle heating, in a mixture of HCl (1:1) (5 ml) and HNO_3 (1:1) (10 ml). Add conc. H_2SO_4 (5 ml), evaporate to fuming, cool, dilute with H_2O to 20 ml and add conc. HCl (20 ml). Dissolve, if necessary by gentle heating, transfer the orange soln. to a 100-ml flask, add conc. HCl (40 ml) and dilute with H_2O to vol. To 10 ml of this soln. add 200 g of zinc amalgam and reduce in a special vessel (illustrated) in which the titration is performed in an inert atmosphere. Remove the amalgam and titrate the soln. potentiometrically with 0·1 *N* $K_2Cr_2O_7$. Three potential changes were observed, corresponding to $Mo^{III} \rightarrow Mo^{V}$, $Mo^{V} \rightarrow Mo^{VI}$, and $Fe^{II} \rightarrow Fe^{III}$. Conditions for the titration of Mo^{III} with $Ce(SO_4)_2$, $KBrO_3$, KIO_3, chloramine T, NH_4VO_3, $(NH_4)_2SO_4.Fe_2(SO_4)_3$, $K_2H_2Sb_2O_7$, $CuSO_4$ and iodine are also described. The composition of the reduced form of Mo^{III} and the mechanism of the oxidation with the soln. used are discussed.

J. ZÝKA

3224. **Solochrome violet R as reagent for the spectrophotometric determination of microgram amounts of molybdenum.** J. Korkisch and M. Osman (II Chem. Inst., Univ. Vienna, Austria).

Z. anal. Chem., 1959, **171** (5), 349–353.—Molybdenum (0·2 to 50 μg) can be determined spectrophotometrically by measuring the extinction at 565 mμ of the red complex formed between Mo and Solochrome violet R (C.I. Mordant Violet 5) (**I**) in 0·1 *N* HCl soln. The effect of concn. of dye on the formation of the red colour of the Mo - **I** complex, pH, time and temperature is discussed. The method described is suitable for the determination of concn. down to 0·2 μg of Mo in 10 ml of soln. *Procedure*—To 5 ml of Mo soln. in 0·1 *N* HCl are added a few crystals of ascorbic acid and, after 5 min., 2 ml of 0·01 *M* EDTA (disodium salt) and 2 ml of 0·01% **I** soln., and the soln. is diluted to 10 ml with 0·1 *N* HCl. A blank is carried out without the sample. The content of Mo is found by reference to a calibration curve. In the presence of EDTA and ascorbic acid, Zr and Fe^{3+}, respectively, do not interfere. No masking agent is necessary for Tl, Al, Zn, Cd or F^-, but SO_4^{2-}, PO_4^{3-}, Cu, Cr and Ni interfere when present in large amounts. Errors of ± 7% for concn. of 2 to 15 μg of Mo and ± 4 to 5% for concn. of 15 to 30 μg of Mo are claimed. B. B. BAUMINGER

3225. **The determination of molybdenum and its application in the hydrometallurgy of copper.** H. R. Skewes (Div. of Mineral Chem., C.S.I.R.O., Melbourne, Australia). *Aust. J. Appl. Sci.*, 1959, **10** (4), 464–469.—The procedure permits from 1 to 25 μg of Mo^{IV} to be determined (with a reproducibility within 0·2 μg) in the presence of a large excess of Cu in an aliquot of a soln. of (*i*) copper concentrate leachate, electrolyte or cathode copper, or (*ii*) slag, tailings, matte or other smelter product. The average recovery of Mo is 98·8% with a mean variation of ± 1·9%. The Mo is pptd. at ≃ 21° as the benzoin α-oxime complex, which is then extracted wite $CHCl_3$ (3 × 5 ml). The solvent is boiled off completely and, after cooling and adding 1 ml of a soln. containing 0·5 mg of Fe per ml, H_2SO_4 (4 ml), $HClO_4$ (6 drops) and HNO_3 (2 drops), the mixture is taken to fuming to destroy the complex. The residual soln. (≃ 3·5 ml) is diluted to ≃ 17 ml with H_2O so that the concn. of H_2SO_4 is ≮ 7 *N*, and the Mo is recovered as the green dithiol complex, which is then extracted into *iso*amyl acetate and its extinction measured at 680 mμ after 4 to 6 hr. W. J. BAKER

3226. **Determination of small amounts of uranium in minerals by the phosphate - vanadate process.** C. Mendonça Pinto, E. Moysés and E. Ribeiro Teixeira (Univ. de Minas Gerais, Brazil). *Fóton*, 1959, **1**, 13–20 (in Portuguese).—The phosphate - vanadate determination of U is based on the pptn. of U^{IV} with sodium phosphate in acid soln. and subsequent titration of U^{IV} with vanadate in conc. H_2SO_4. In the phosphate pptn., all elements are removed except Zr, Ti and Th, and these do not interfere with the titration. In the process the ore is leached in HCl, and the sodium phosphate is added to the soln. The U is pptd. with Zr, Ti and Th, but all other elements remain in soln. The ppt. is then dissolved in H_2SO_4 and titrated with NH_4VO_3 soln., with N-phenylanthranilic acid as indicator. The results obtained show that the method is simple and precise for the determination of small amounts of U in minerals and ores.
NUCL. SCI. ABSTR.

3227. **Determination of small amounts of uranium in rocks and rock phosphates.** G. Jangg, W. Ochsenfeld and F. Habashi (Inst. f. chem. Technol. anorg. Stoffe, Wien, Austria). *Z. anal. Chem.*, 1959, **171** (1), 27–37.—The separation of U from accompanying metals is achieved by passing a soln. of the sample in H_2SO_4 (pH 1·5) containing 10 ml of a satd. SO_2 soln. through a column of Amberlite IRA-400 pre-treated with 0·1 *N* H_2SO_4; the U is eluted with 0·8 *N* HCl. With very impure soln., the eluate is evaporated to dryness, the residue is dissolved in 100 ml of acetate buffer soln. (4·2 g of Na acetate and 1 ml of glacial acetic acid in 1 litre of H_2O) and passed through a second column of Amberlite IRA-400 pre-treated with buffer soln. The U is again eluted with 0·8 *N* HCl and determined polarographically as the nitrate. By the procedure described, microgram amounts of U can be separated with a precision of ± 10%. Separations of U from MoO_4^{2-}, WO_4^{2-} and PO_4^{3-} are described. B. B. BAUMINGER

3228. **A specific method for the determination of uranium in ores by cathode-ray polarography.** T. M. Florence (Australian Atomic Energy Comm., Res. Estab., Lucas Heights, N.S.W.). *Anal. Chim. Acta*, 1959, **21** (5), 418–424.—The ore is dissolved in conc. HNO_3 + HF and the soln., which should be 10^{-5} to 2×10^{-4} *M* in U, is adjusted to 0·1 *M* in $HClO_4$. The U is first separated from the bulk of Cu, Fe, Mo, Sn and other metals by electrolysis at 6 to 9 V (1·5 amp.) for 40 to 60 min. in a small mercury-cathode cell, and is then determined, in the presence of a basal electrolyte, by cathode-ray polarography at 25° in a cell having a mercury-pool anode against which the peak current is measured at −0·28 V. A blank is run with a standard soln. of UO_2Cl_2 of approx. the same concn. as the unknown, and a correction is made for residual current (< 0·01 mA). The basal electrolyte [0·2 *M* ascorbic acid - 0·4 *M* ammonium citrate - 0·2 *M* citric acid - 0·05 *M* ammonium oxalate - 0·05 *M* EDTA (disodium salt) - 0·05 *M* NaCl] obviates interference from V, Ti and W. The accuracy is within ± 1·4% for ores containing ≮ 0·5% of U_3O_8, but decreases considerably for lower concn. The coeff. of variation is ± 1·9% (10 analyses). (*Cf. Australian Atomic Energy Comm.*, Rep. AAEC/E-39, 1959.) W. J. BAKER

3229. **Simple determination of uranium in graphite.** R. N. Rogers (Los Alamos Sci. Lab., N. Mex., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2071–2072.—The sample (containing 0·05 to 0·4 g of U) is decomposed by digestion for ≃ 3 hr. with 25 ml of a mixture of equal vol. of H_2SO_4, HNO_3 and $HClO_4$ (this acid is replenished as necessary). The soln. is cooled and the U is then determined by direct colorimetry at 420 mμ, against standard curves for 10^{-4} to 2×10^{-3} *M* ^{238}U. The accuracy and precision are high, depending mainly on the degree of uniformity of the graphite pieces. The method is suitable for routine analyses of graphite fuel elements and of "green mixes" (coke, pitch and C). W. J. BAKER

3230. **Spectrographic determination of uranium or its compounds in the presence of impurities by diffusion - convection transference.** V. F. Prokof'ev, N. S. Sventitskiĭ and K. I. Taganov. *Fiz. Sb. L'vov. Univ.*, 1958, [4 (9)], 42–44, *Ref. Zhur., Khim.*, 1959, (19), Abstr. No. 67,720.—In order to eliminate the overlapping of uranium spectra on a very dense background the impurities should be removed during the spectrographic process by transfer to a supporting graphite electrode; the graphite electrode carrying the sample (converted into U_3O_8) is

heated by a d.c. subsidiary arc. The electrode carrying the sample serves as the anode; two carbon cathodes are arranged symmetrically at right angles to it. By operation of the subsidiary arc the impurities are transferred to the auxiliary upper electrode, but the non-volatile U_3O_8 remains on the lower electrode. Such a transfer is called "diffusion - convection." The U_3O_8 sample (50 mg to 200 mg, depending on the amount of impurities present) is mixed with 2% of carrier (AgCl or NH_4Cl) and placed in the bore of the lower electrode which is covered with a graphite lid, 0·8 mm internal diameter. The subsidiary arc (10 amp.) for heating burns at the circumference for 1 min. The electrode carrying the sample is then replaced by a pointed graphite electrode and the spectra of the transferred impurities are excited in an a.c. arc and photographed. The determination of the impurities is carried out by means of the most persistent lines; Mn serves as the internal standard and is added as the nitrate to a concn. of 1%. Synthetic standards are prepared from U_3O_8 of known chemical composition. The method is highly sensitive; Cd lines are detected at a concn. of $< 5 \times 10^{-6}$ %. K. R. C.

3231. **Precision mass-spectrometric determination of uranium isotopic composition.** G. F. Kauffman and C. D. Tabor (Goodyear Atomic Corp., Portsmouth, Ohio). *U.S. Atomic Energy Comm.*, Rep. GAT-T-664, May, 1959. 16 pp.—Mass spectrometers are subject to a variable phenomenon called "memory" which amounts to 1 to 20% in the analysis of UF_6. A procedure with the use of an interpolative method of standardisation reduces the effect of memory to a negligible amount, while at the same time compensating for or eliminating other sources of error. The use of a mass spectrometer for the rapid and accurate determination of uranium isotopic abundance is described.

Nucl. Sci. Abstr.

3232. **Spectrographic determination of uranium-235. I. Photographic recording and d.c. arc excitation.** T. Lee, A. L. Hallowell and L. H. Rogers (Gaseous Diffusion Plant, Union Carbide Nuclear Co., Oak Ridge, Tenn.). *Appl. Spectroscopy*, 1960, **14** (2), 39–41.—This first report summarises one aspect of work carried out prior to 1950 at the Oak Ridge Gaseous Diffusion plant, on the development of a spectrographic d.c. arc technique for the determination of ^{235}U. A short review of spectroscopic work on uranium isotopes is given; the experimental work is concerned with a statistical examination of the effect on the precision of determinations of ^{235}U over a content range of 0·5 to 93·0% of such factors as spectrograph slit widths, slit types and different spectral line pairs used for analysis. By using optimum analytical conditions in the range 0·5 to 1·5% of ^{235}U, at the natural ^{235}U level of $\simeq$ 0·71%, a precision of 0·04 % by wt. of ^{235}U with a 95% probability is claimed.

G. P. Mitchell

3233. **Determination of traces of certain rare-earth elements in uranium compounds by ion exchange and spectrography.** J. A. Carter and J. A. Dean (Diffusion Plant, Union Carbide Co., Oak Ridge, Tenn.). *Appl. Spectroscopy*, 1960, **14** (2), 50–52.—In the analytical control of elements of high cross-section for thermal neutron capture (Dy, Eu, Gd and Sm) in uranium and its compounds, Dowex 50–X8 cation-exchange resin is used to separate the cationic rare-earth fluorides from the anionic uranyl fluoride complex occuring in fluoride soln. of uranium. A study of the distribution coeff. in the resin, and of the elution of U, gives the optimum HF concn. and elution vol. for a 95% efficient separation. After separation the resin is ashed at 800°, mixed with graphite and the analysis is completed spectrographically, with d.c. arc excitation and yttrium as the internal standard; 0·01 to 100 p.p.m. of Dy, Er, Eu, Gd, Nd, Sm and Yb in uranium may be determined.

G. P. Mitchell

3234. **Determination of trace amounts of nickel in uranium.** V. T. Athavale, L. M. Mahajan, N. R. Thakoor and M. S. Varde (Atomic Energy Estab., Trombay, Bombay, India). *Anal. Chim. Acta*, 1959, **21** (5), 491–492.—From 5 to 100 μg of Ni in $\simeq$ 1 g of U_3O_8 can be determined colorimetrically with dimethylglyoxime in a soln. containing ammonium carbonate and ammonium citrate as complexing agents (for U, Th, Fe and other metals) and adjusted to pH 11·5 $\pm$ 0·5. The extinction is measured after $\simeq$ 30 min. at 530 mμ in a 1-cm cell; the colour is stable for at least 24 hr. Concn. as low as 1 p.p.m. of Ni can be determined if a 5-cm cell is used; Cu^{2+}, Co^{2+} and Cr^{3+} interfere slightly at concn. $>$ 50 to 100 μg. W. J. Baker

3235. **Determination of metallic impurities in uranyl nitrate solutions by X-ray fluorescence.** R. E. Sladky (Union Carbide Nuclear Co. Y-12 Plant, Oak Ridge, Tenn.). *U.S. Atomic Energy Comm.*, Rep. Y-1276, March, 1959. 25 pp.—An X-ray fluorescence spectrometer was used to measure the concn. of Fe. An estimate of the U concn. was obtained simultaneously. The sensitivity of the fluorescence method for eleven other metals was obtained. Nucl. Sci. Abstr.

3236. **Determination of fluorine in the presence of some interfering ions.** V. P. Hirsjärvi, E. Kenttämaa, M. Suurinkeroinen, B. Aimonen and R. Martti (State Agric. Chem. Lab., Helsinki, Finland). *Z. anal. Chem.*, 1959, **171** (5), 354–359.—A modification of the distillation apparatus of Willard and Winter (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 7) is described, which allows the removal of milligram amounts of F in mineral feeds and rock phosphates. Fluorine in the distillate is titrated with thorium nitrate soln. (0·02 *N*), with sodium alizarinsulphonate soln. (0·025%) as indicator. It is shown that the method is not affected by the presence of SO_4^{2-}, Cl^- and PO_4^{3-}, and the interference from BO_3^{3-} and CO_3^{2-} is small.

B. B. Bauminger

3237. **Amperometric determination of fluorine in etching baths.** V. F. Mal'tsev and V. P. Novak (Ukrain. Sci. Res. Tube Inst.). *Zavod. Lab.*, 1959, **25** (11), 1296–1297.—Titration is carried out with $FeCl_3$ soln., a rotating platinum electrode and a S.C.E. To determine the free F^-, 5 ml of the diluted soln. (5 ml of the electrolyte diluted to 100 ml) is mixed with 5 ml of ethanol and 1 to 2 g of NaCl and treated with 2% HNO_3 soln. or 2% NaOH soln. to give a pH of between 5 and 6. The soln. (20 ml) is titrated with $FeCl_3$ soln. (0·010 to 0·012 g of Fe per litre) at a potential of 0·5 V. To determine the total content of F^-, 5 ml of the electrolyte is diluted with water and treated with 10 ml of 20% NaOH soln. After being heated at 50° to 70°, the soln. is cooled and diluted to 100 ml. A filtered aliquot (5 ml) is titrated to give the content of F^-. The error is $\simeq$ 1% of the content. G. S. Smith

3238. **Studies in the spectrophotometric determination of silicon in materials decomposed by hydrofluoric acid. II. Determination of fluorosilicic acid in hydrofluoric acid.** P. R. Graff and F. J. Langmyhr (Oslo Univ., Blindern, Norway). *Anal. Chim. Acta*, 1959, **21** (5), 429–431.—To a weighed amount of sample ($\simeq$ 1 ml) in a plastic beaker are added 25% aq. $AlCl_3$ (50 ml) and 2% ammonium molybdate soln. (5 ml), and the mixture is diluted to $\simeq$ 90 ml with H_2O. The pH is then adjusted to 1·0 $\pm$ 0·5, the soln. is heated at 100° for 3 hr. (steam bath), cooled and made up to 100 ml. The extinction is then measured at 370 mμ against the reagent blank. Beer's law is followed up to 0·8 mg of SiO_2 per 100 ml; $AlCl_3$ is better than H_3BO_3 for complexing the excess of HF because the compound formed does not attack glass.

W. J. BAKER

3239. **Complexometric determination of fluoride in cryolite.** Ya. G. Sakharova and N. I. Shishkina (Ural Sci. Res. Inst. of Ferrous Metals). *Zavod. Lab.*, 1959, **25** (12), 1442–1443.—The sample (0·25 g) of cryolite is fused at 900° to 1000° for 20 min. with 0·25 g of quartz sand and 6 g of K_2CO_3 - Na_2CO_3. The melt is heated with water and an aliquot (100 ml) of the soln. (250 ml) is made just acid to methyl orange indicator with HNO_3 (1 : 1), then treated with 10 drops of glacial acetic acid and 30 ml of 5% NaCl soln. and mixed at 40° to 50° with 50 ml of 2·5% Pb acetate soln. from a burette. After 3 to 5 min. an aliquot (50 ml) of the diluted (250 ml) and filtered soln. is mixed with 10 ml of 5% tartaric acid soln. to retain Pb in soln., 10 ml of 25% aq. NH_3 and 2 to 3 drops of 0·5% chromogen black ET-00 (C.I. Mordant Black 11) soln., and titrated with 0·05 *N* EDTA (disodium salt) to give the amount of Pb in excess of that required to form PbClF.

G. S. SMITH

3240 **Lanthanum chloranilate. A direct colorimetric reagent for general fluoride determinations.** L. Fine and E. A. Wynne (Res. and Development Sect., Fisher Scientific Co., Fair Lawn, N.J., U.S.A.). *Microchem. J.*, 1959, **3** (4), 515–522.—Fluoride ions react with insoluble lanthanum chloranilate to form lanthanum fluoride and an equivalent amount of free chloranilic acid, which is determined photometrically. *Procedure*—With inorganic materials, remove cations from the sample soln. by ion exchange with Amberlite IR-120 resin. With organic fluorides, use a soln. from a suitable combustion procedure. To an aliquot containing 2 to 200 μg of F^- add Na acetate - acetic acid buffer (pH 4·6) (10 ml). Dilute the soln. to 100 ml with 50% aq. 2-methoxyethanol, add solid lanthanum chloranilate (0·2 g), and shake immediately. Then set aside the flask for 30 min., but shake at 3-min. intervals. Filter or centrifuge the mixture until the filtrate is clear, and measure the extinction at 530 mμ against a blank. No common anions, except phosphate and molybdate, interfere at the concn. tested. The procedure has a precision of $\simeq$1%.

W. T. CARTER

3241. **Determination of chlorine in silicate rocks.** L. C. Peck and E. J. Tomasi (U.S. Geol. Survey, Denver, Colo.). *Anal. Chem.*, 1959, **31** (12), 2024–2026.—The sample (0·5 g) is sintered at $\simeq$ 800° for 30 min. with a mixture of Na_2CO_3, ZnO and $MgCO_3$ (7 : 2 : 1) (5 g). The sinter cake is leached with H_2O (30 ml), the soln. is filtered and the filtrate is diluted to 90 ml. Three drops of 3% H_2O_2 and 10 ml of HNO_3 are added, and the soln. is then titrated with 0·01 *N* $Hg(NO_3)_2$, with 10% aq. sodium nitroprusside soln. as internal indicator. The titration is made in darkness with a beam of light shining through the soln., and the end-point is found by visually comparing the intensity of this beam with that of a similar beam passing through a standard turbid soln. The addition of one drop in excess of titrant at the end-point makes the beam in the sample soln. much brighter than the reference beam when the soln. has been stirred for several minutes. A blank is run to correct for Cl in the flux. If the sample is ground to 80 mesh and the content of Cl is $<$ 0·2%, the accuracy is equal to that of the AgCl method. The occasional sample containing $>$ 0·2% of Cl should be re-analysed after grinding it more finely. The sensitivity is $\simeq$ 0·01% of Cl, and 12 analyses can be completed per day; Br and I interfere.

W. J. BAKER

3242. **Determination of chloride in sulphite waste liquor.** O. Lagerström and O. Samuelson (Res. Lab., Mo & Domsjö AB, Örnsköldsvik, Sweden). *Svensk Papp-Tidn.*, 1959, **62** (19), 679–680 (in English).—The Cl^- are retained on an anion-exchange column. After elution with NH_4NO_3 soln. the interfering thiosulphate and polythionate ions are destroyed by oxidation with H_2O_2 in alkaline medium, and Cl^- are then determined by potentiometric titration with $AgNO_3$ soln. Dowex-2 resin (NO_3^- form) (0·12 to 0·30 mm) is used in a column of diameter 10 mm and height 150 mm. *Procedure*—Pass the sample (50 ml) through the column at a flow rate of 2·5 ml per min. Wash the resin with water (50 ml) and then elute with 5 *M* NH_4NO_3 (100 ml). Add NaOH (0·1 g) and H_2O_2 soln. [30% (w/v), 2 ml], heat to boiling and set aside on a steam bath for 45 min. Cool, add HNO_3 (5 ml) and titrate with 0·02 *N* $AgNO_3$, with a silver electrode and a S.C.E. connected through an NH_4NO_3 - agar bridge. Good recovery of NaCl added to waste liquor is reported; the reproducibility is claimed to be good.

B. RÖNNHOLM

3243. **Coulometric estimation of periodate.** H. L. Kies and J. J. Buyk (Tech. Hoogschool, Delft, Netherlands). *J. Electroanal. Chem.*, 1959, **1** (2), 176–180.—In a soln. containing $Fe_2(SO_4)_3$ (0·1 *M*) and H_2SO_4 (0·5 *M*), KIO_4 (0·06 to 15 mg) can be determined coulometrically. A 25-fold excess of IO_3^- does not interfere; a larger proportion causes inaccuracies.

E. G. CUMMINS

3244. **Determination of manganese oxides of various valencies.** J. Babčan (Inst. Mineral Raw Materials, Kutná Hora, Czechoslovakia). *Hutn. Listy*, 1959, **14** (12), 1084–1086.—The following procedures for the determination of a mixture of manganese oxides are recommended. *Procedure for MnO*—To the sample ($\geqslant$ 0·05 g of MnO) add 3 *M* $(NH_4)_2SO_4$ (50 ml) and heat on a water bath for 1 hr., with stirring at 10-min. intervals. Filter off the undissolved residue, wash with hot H_2O and determine Mn in the filtrate. If alkaline earths are present, the dissolution and filtration must be carried out in an inert atmosphere. The determined amount corresponds to the MnO content, but includes also a small part of the Mn_2O_3 and a larger amount of Mn from $MnCO_3$. In the undissolved residue MnO_2 is determined. The difference between the total MnO_2 determined directly (see below) and the MnO_2 determined in the residue corresponds to the Mn_2O_3 decomposed by $(NH_4)_2SO_4$. *Procedure for MnO_2*—To the sample ($\geqslant$ 0·04 g of MnO_2) add KI (0·5 g), 0·1 *M*

EDTA (disodium salt) (10 ml), Na acetate (0·5 g) and acetic acid (5%) (10 ml) and mix in a closed flask for 7 min. Dilute with H_2O and titrate with $Na_2S_2O_3$ soln. *Procedure for* Mn_2O_3—Dissolve the sample (0·08 to 0·1 g of Mn_2O_3) by heating on a water bath with HNO_3 (1%) (60 ml) for 1 hr. Filter off the undissolved residue, wash with hot H_2O and determine Mn^{3+} in the filtrate. The total amount of Mn found corresponds to that from the MnO and one half of that from the Mn_2O_3. Transfer the filter with the undissolved residue to a flask and determine MnO_2 as described above. The difference between the present amount and that determined directly by the above procedure corresponds to the second half of the Mn from Mn_2O_3. The determination of Mn_2O_3 can also be carried out by heating the sample on a water bath for 1 hr. in a mixture of $Na_4P_2O_7$ (10%) (100 ml) and H_2SO_4 (1:1) (2 ml), filtering, adding a known vol. of 0·01 *M* $(NH_4)_2SO_4.FeSO_4$ and titrating the excess manganometrically. *Procedure for* Mn_3O_4—By decomposing the sample with HNO_3, Mn^{3+} are liberated from MnO, Mn_2O_3 and Mn_3O_4; MnO and Mn_2O_3 are determined as described above, and Mn_3O_4 obtained by difference. J. ZÝKA

3245. **Polarographic determination of microgram amounts of rhenium.** K. S. Pakhomova and L. P. Volkova (All-Union Inst. of Mineral Raw Materials). *Zavod. Lab.*, 1959, **25** (11), 1291–1292.—In NaOH soln. (1 to 5 *N*) containing Na_2SO_3 (0·1 to 2 g in 25 ml) Re gives a well-defined polarographic wave with $E_{\frac{1}{2}} = -1{\cdot}4$ V and the wave height is proportional to concn. The method is sensitive to 0·2 μg of Re. With molybdenite, contents of Re between 10^{-4} and 0·5% can be determined by use of a sample wt. of between 3 and 0·05 g. Separation of Re from Mo is carried out by the method of Ranskiĭ (*Anal. Abstr.*, 1959, **6**, 1732). Small amounts of Mo (> 0·2 mg per ml) and Cr (> 0·001 mg per ml) and amounts > 1 mg of Fe, Mn, As, Sb, Bi, Se, Co or W per ml do not interfere. With 1 to 2 μg of Re per ml and 0·4 to 0·5 g of Na_2SO_3 in 25 ml a max. appears on the wave. This can be suppressed by increasing the content of Na_2SO_3 to 2 g if the content of Re is > 5 μg per ml. With higher contents of Re the addition of gelatin is necessary. G. S. SMITH

3246. **Potentiometric determination of rhenium in the presence of molybdenum.** D. I. Ryabchikov, V. A. Zarinskiĭ and I. I. Nazarenko (V. I. Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (6), 737–738.—The reduction potential for $Re^{VII} \rightarrow Re^{IV}$ varies from + 0·234 V in *N* H_2SO_4 to + 0·461 V in 15 *N* H_2SO_4 (*vs.* the S.C.E.); a clear brown colloidal soln. of $ReO_2.nH_2O$ is obtained. A method for determining Re in the presence of an approx. equal amount of Mo is developed, based on the titration of perrhenate with Cr^{2+} in 4 *N* to 12 *N* H_2SO_4 (platinum indicator electrode). In the determination of 7·77, 9·71 and 12·62 mg of Re in the presence of 11·32 mg of Mo, the amounts of Re found were 7·90, 9·30 and 13·00 mg, respectively. C. D. KOPKIN

3247. **Analytical use of 8-mercaptoquinoline (thio-oxine) and its derivatives. VIII. New photometric determination of rhenium in the presence of molybdenum, tungsten and other elements.** Yu. A. Bankovskiĭ, A. F. Ievin'sh and E. A. Luksha (Institute of Chemistry, Academy of Sciences, Latvian SSR, Riga). *Zhur. Anal. Khim.*, 1959, **14** (6), 714–720.—In soln. 5 to 11·5 *N* in HCl, thio-oxine (**I**) forms with $KReO_4$ a stable complex, which is readily soluble in $CHCl_3$; the higher the acidity, the greater the selectivity for Re. The $CHCl_3$ soln. has maximum absorption at 438 mμ; the calibration curve (5 to 200 μg of Re in 5 ml of $CHCl_3$) has only a slight deviation from the rectilinear. To determine Re, add to the test soln. (8 ml) in a 100-ml flask 37 ml of conc. HCl, mix, add 5 ml of a 6% soln. of **I** in conc. HCl, place the flask on a boiling-water bath for not more than 3 min., cool immediately, transfer the soln. to a 100-ml separator, and extract the rhenium complex by shaking with 5 to 10 ml of $CHCl_3$. Separate the $CHCl_3$ layer, transfer it to another separator containing 22 ml of 9 *N* HCl, shake for 2 min., add 2·5 ml of **I** soln., shake for a further 2 or 3 min., transfer the $CHCl_3$ layer to a test-tube, dry it for 1 or 2 min. with 1 or 2 lumps of anhyd. $CaCl_2$ (which should not have an alkaline reaction), and measure the extinction in a 1-cm cell at 438 mμ. Find the content of Re from the calibration curve, obtained analogously. Tables of the effects of the presence of other elements are given. C. D. KOPKIN

3248. **Recovery of rhenium and the analysis of its alloys.** A. A. Woolf (Ass. Electr. Ind., Aldermaston, Berks., England). *J. Less-Common Metals*, 1959, **1** (6), 420–423.—Rhenium in most alloys is readily volatilised as Re_2O_7 which can be dissolved in water and titrated with standard alkali. The apparatus consists of a horizontal silica tube containing the sample (alone or in a platinum-foil capsule) joined to a 500-ml bulb. The bulb is evacuated and filled with O at 1·3 atm., and the silica tube is maintained at 1000° until oxidation is complete. The silica tube is cut below the sublimed layer of Re_2O_7, which is dissolved in water and titrated with NaOH to methyl red. Alternatively, spectrophotometric analysis at 210 mμ is possible (*cf.* Headridge, *Analyst*, 1958, **83**, 690). N. E.

3249. **Photometric determination of small quantities of iron with picolinaldoxime.** H. Hartkamp (Inst. für Spektrochemie und angew. Spektroskopie, Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 1959, **170** (2), 399–407 (in German).—The reagent forms an intense, red, water-soluble complex with Fe^{II} in the pH range 10 to 13. The reaction is sensitive, the complex is stable and, with a few exceptions, is unaffected by the reducing agent used to convert the iron into the bivalent state. Vanadium, Cr, Co, Ni, Mn and Cu interfere if present in concn. > 10 μg per ml. Tartaric and citric acids can be used to prevent ppt. formation, but EDTA causes low results. For concn. between 0·5 and 5·0 μg of Fe per ml the coeff. of variation is < 1%. W. T. CARTER

3250. **Phenyl 2-pyridyl ketoxime, a reagent for iron in strong alkalis. A method for determining oxidised iron in the presence of metallic iron.** F. Trusell and H. Diehl (Dept. of Chem., Iowa State Univ., Ames, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1978–1980.—In a strongly alkaline soln. (pH 9 to 11), phenyl 2-pyridyl ketoxime (**I**) (0·2% in 0·1 *N* HCl) reacts directly with Fe^{3+}; "oxidised" Fe (*i.e.*, in the haematite or magnetite form) (in the p.p.m. range) in alkali-metal hydroxides, sodium carbonate and sand (after fusion with Na_2CO_3 - $Na_2B_4O_7$) can be determined colorimetrically after reduction. Iron-free $Na_2S_2O_4$ (10% aq.

soln.) is the preferred reducing agent. The Fe^{3+}-**I** complex is extracted once with *iso*amyl alcohol containing a few ml of ethanol, and the extinction of the red soln. is measured at 550 mμ. Beer's law holds for concn. $> 10^{-4}$ *M*; the molar extinction coeff. is 15,600. Low results are obtained for the content of Fe in lithium and sodium hydroxides, indicating that the Fe is present in two forms.

W. J. BAKER

3251. **Heterometric micro-determination of trace amounts of iron in thiocyanate solutions by titration with nitron.** M. Bobtelsky and A. H. I. Ben-Bassat (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1959, **21** (5), 411–415.—Less than 0·1 mg of Fe^{3+} in 20 ml of soln. can be determined heterometrically, in ≃ 5 min., in the presence of ≃ 0·1 g of Ca^{2+}, Ba^{2+}, Mg^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, Mn^{2+}, Cd^{2+}, Th^{4+}, Ce^{3+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, MO_4^{2-}, VO_3^-, Sb^{3+} or WO_4^{2-}. The titration is made with a 0·0025 to 0·0033 *M* soln. of nitron in the presence of 2 *M* KSCN (5 ml), *M* citric acid (1 ml) and *N* HCl (0·5 ml). The error is usually ≃ 1%; the molar ratio of Fe to nitron at the end-point always 1:6·6.

W. J. BAKER

3252. **Determination of iron and manganese by atomic absorption.** J. E. Allan (Dept. of Agric., Rukuhia Soil Res. Sta., Hamilton, N.Z.). *Spectrochim. Acta*, 1959, (10), 800–806.—A single-channel direct-reading attachment to a Hilger medium spectrograph was adjusted to record either Fe 2483·3 A or Mn 2794·8 A, which were found to be the most sensitive lines for atomic absorption determinations. Solutions were prepared from samples of soil, soil extracts and plants and sprayed into an air-acetylene flame from a modified Lundegårdh atomiser. It was important to standardise the type of acid and concentration to obtain uniform atomisation rates, but no interference from large variable additions of K, Ca, Na, Mg and P to the solutions was observed. Several types of hollow-cathode manganese lamp were tried in order to obtain improved line-to-background ratios. Coeff. of variation of ≃ 4·0 were obtained over the ranges 2·5 to 125 p.p.m. of Fe and 0·5 to 25 p.p.m. of Mn.

P. T. BEALE

3253. **Determination of ferrocyanides in the presence of ferricyanides, cyanides and thiocyanates. Gravimetric method.** S. Arribas Jimeno (Univ. de Oviedo, Spain). *Inf. Quim. Anal.*, 1959, **13** (6), 167–174.—Ferrocyanides are pptd. as $(NH_4)_4Fe(CN)_6.2MoO_3$, which is weighed after drying at 120°. The ppt. loses HCN at higher temp. *Procedure*—To the neutral soln. containing > 0·300 g of $K_4Fe(CN)_6$ add 50 ml of NH_4Cl soln. (30%, w/v) and 10 ml of acetate buffer soln. (pH 3·7) and dilute to 100 ml with water. Add sufficient $(NH_4)_2MoO_4$ soln. (0·1 *N*) to precipitate the ferrocyanide and leave the mixture to stand for several hours. Filter off the ppt. on a No. 3 sintered glass crucible and wash first with NH_4Cl soln. (15%, w/v) and then with 50% ethanol. Dry for 2 hr. at 120° to constant weight. This method gives results within ± 1% of the calculated values.

G. H. FOXLEY

3254. **Direct determination of aluminium in iron ores after a simultaneous separation of iron and titanium.** F. G. Zharovskiĭ. *Ukr. Khim. Zhur.*, 1959, **25** (2), 245–248; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,300.—The pH range for the interaction of N-benzoyl-N-phenylhydroxylamine (**I**) with the cations of the third and fourth analytical groups and the conditions for the extraction with $CHCl_3$ of the compounds formed have been determined. The separation of Fe and Ti from Al by the $CHCl_3$ extraction of their compounds with **I** has been achieved, and a new method for the direct determination of Al, after separating Fe and Ti by extraction, has been developed. Highly satisfactory results were obtained when the method was tested on synthetic mixtures and standard samples of iron ores.

W. ROUBO

3255. **Spectrographic analysis of solutions on the Steelometer ST-7.** V. D. Pisarev and N. P. Vasil'ev (Novosibirsk Inst. of Soviet Co-operative Trade). *Zavod. Lab.*, 1959, **25** (12), 1454–1455.—A stream of N carries the atomised soln. into the gap between two carbon electrodes disposed horizontally, subjected to a condensed spark discharge. The spectrum is examined visually, without photographic recording, in a Steelometer. The errors with contents of Mg between 0·0025 and 0·0073%, of Ca between 0·005 and 0·05%, and of Sc between 0·005 and 0·05% correspond with those usually obtained photographically.

G. S. SMITH

3256. **Sampling liquid steel for hydrogen.** J. G. Bassett. *Proc. Amer. Inst. Min. Engrs Nat. Open Hrth Comm.*, 1958, **41**, 80–89.—A method is described for obtaining a steel sample for H content directly from the bath. It involves the use of an evacuated Pyrex-glass tube containing a copper mould. The technique is compared with those of the Taylor sampler and the Geffner pin tube and is shown to give consistently higher H contents. The use of the sampler in studying trends of H in acid open-hearth steel is reported.

J. IRON ST. INST. ABSTR.

3257. **Spectrographic micro-analysis of high-alloyed steels and heat-resisting alloys.** A. G. Komarovskiĭ. *Fiz. Sb. L'vov. Univ.*, 1958, [4 (9)], 404–406; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,348.—For the determination of the chemical composition of thin surface layers of cracks formed during forging of steels and alloys, the spectra of the samples are excited by spark discharge with a capacitance of 0·0023 μF, zero self-inductance and a 1-mm spark gap. The counter-electrode of 9 mm diam. is prepared from electrolytic copper shaped into a truncated cone. The spectra are photographed for 60 sec. During the study of heat-resisting alloys a considerably higher concn. of Mo and Ti (1·1 times as great) and also Al and Nb (1·5 to 2 times) was observed on the surface of cracks as compared with the concn. of these elements in the base metal.

W. ROUBO

3258. **Simultaneous spectrophotometric determination of copper and nickel in low-alloy steels.** M. Freegarde and B. Jones (Bragg Lab., Naval Ordnance Inspect. Estab., Janson St., Sheffield, England). *Analyst*, 1959, **84**, 716–719.—The sample is dissolved in a mixture of 25% (v/v) H_2SO_4 and 40-vol. H_2O_2 and the H_2O_2 is removed by boiling. To an aliquot of the filtered soln. are added an aq. NH_3-ammonium citrate buffer soln. (pH 10 ± 0·1) and specified amounts of soln. of bis*cyclo*hexanoneoxalyldihydrazone and disodium ethyl di-(5-tetrazolylazo)acetate. The extinction of the suitably diluted liquid is measured at 510 and 600 mμ against a blank soln. similarly prepared from pure iron. The extinctions are referred to a calibration net, the preparation of which is described.

A. O. JONES

3259. **Colorimetric determination of magnesium in cast iron.** A. K. Babko and N. V. Lutokhina. *Ukr. Khim. Zhur.*, 1959, **25** (2), 226–229; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,296.—The photometric determination of Mg based on the formation of coloured adsorption compounds of $Mg(OH)_2$ with Titan yellow and Magneson II has been studied, and the optimum conditions and relative amounts of Mg and reagents have been determined. The method has been applied to the determination of Mg in various types of cast iron. The procedure involves the separation of Fe by complexing it with 1-nitroso-2-naphthol and extracting the complex with $CHCl_3$; Mg is determined in the aq. phase. W. ROUBO

3260. **Spectrographic determination of aluminium in alloyed steels by a solution technique.** Yu. Ya. Kolbovskiĭ and M. K. Krizhanovskaya. *Fiz. Sb. L'vov. Univ.*, 1958, [4 (9)], 402–403; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,301.—*Procedure*—Dissolve 1 g of steel in aqua regia, dilute to 50 ml and to a 10-ml aliquot add 0·5 g of metallic zinc and 0·25 g of NaCl, then immerse a carbon electrode in the soln. for 5 min. The spectra are excited by an a.c. arc at 4 amp. with an upper carbon electrode, and are photographed in a medium spectrograph. A graph of log (I_1/I_2) *vs.* log C is prepared by using the lines Al 3082·2 - Zn 3072·1 A. Addition of NaCl increases the slope of the graph. W. ROUBO

3261. **Spectrochemical determination of carbon in steel and grey cast iron.** R. Plathe and G. Beinroth [Prüfdienststelle 422, Halle (Saale), Germany]. *Chem. Tech., Berlin*, 1959, **11** (11), 587–593.—The emission-spectrographic determination of C (0·05 to 5%) in steel and grey cast iron in spectrographs of moderate dispersion is suitable for routine control purposes. The C line at 2296·89 A is used with Fe (2298·23 or 2279·92 A) as internal standard. The sample is used as the lower electrode and copper as the upper electrode. The accuracy for 0·1 and 1·0% of C is ± 8·5 and ± 3·6%, respectively. Nickel (> 1%) interferes. For amounts of C < 0·1% a graphical correction is applied. The influence of the previous heat treatment of the sample, and of the CO_2 content of the air, is discussed. J. P. STERN

3262. **Rapid determination of phosphorus in steels high-alloyed with chromium and nickel.** B. Kysil and J. Vobora (SONP, Kladno, Czechoslovakia). *Hutn. Listy*, 1959, **14** (12), 1081–1084.—The sample is dissolved and oxidised with perchloric acid, and phosphorus is determined as molybdenum blue. *Procedure*—Dissolve the sample (0·1 g) in $HClO_4$ (d = 1·56) (6 ml) by heating to fumes and heat for a further 6 min. Cool, dilute with H_2O (20 ml) and add Na_2SO_3 soln. (15%) to reduce Cr. Boil for 30 sec. and filter into a 50-ml flask. Add $HClO_4$ (d = 1·56) (6·0 ml), cool, dilute to vol., mix and transfer 25 ml to a 50-ml flask; add ammonium molybdate soln. (5%) (7·5 ml) and dilute with H_2O to 45 ml. After 1 min. add a soln. of $SnCl_2$ (1·5%) (1·5 ml), dilute to vol., and after 4·5 to 5·5 min. measure the extinction at 725 mμ. Compare with a blank. The determination can be carried out in the presence of Cr, Ni, Co, Si, W, Ta, Nb, As, Mo and Ti (≃ 0·5%). J. ZÝKA

3263. **Spectrographic determination of the association between the distributions of phosphorus and arsenic in steel.** E. F. Nikiforova. *Fiz. Sb. L'vov. Univ.*, 1958, [4 (9)], 439–441; *Ref. Zhur., Khim.* 1959, (19), Abstr. No. 67,712.—Spectra are excited in a 14-amp. a.c. arc, with a carbon electrode, for the simultaneous determination of As and P in steel with the lines P 2149·1 - Fe 2150·18 A and As 2288·1 - Fe 2282·1 A. The results of spectrographic determinations are in good agreement with those obtained by chemical methods. K. R. C.

3264. **Spectrographic determination of tantalum and niobium in 18/8 stainless steels.** M. Neuilly. *Mem. Sci. Rev. Métall.*, 1959, **56**, 489–490.—Tantalum and niobium are chemically separated from the steel by standard techniques. A Feussner spark source and a medium dispersion spectrograph are used for the spectrographic determination. The samples are compared with synthetic standards. The typical deviation calculated for concn. between 0·03 and 0·25% was ± 0·01%. NUCL. SCI. ABSTR.

3265. **Turbidimetric titration of cobalt ion with dithio-oxamide.** I. V. Tananaev and L. M. Shapiro. *Sb. Nauch. Rabot. Belorussk. Politekh. Inst.*, 1958, **63**, 159–163; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,321.—By measuring the light absorption of a series of mixtures of $CoCl_2$, dithio-oxamide and H_2O with a variable amount of one component while maintaining the others constant, the formation of $Co_2(C_2H_2N_2S_2)_3$, which is the sole reaction product, has been confirmed. The composition of this compound is not affected by an excess of any of the components of the reaction. In the presence of a stabiliser, a stable, intensively coloured (golden-brown) sol is obtained. On the basis of the results obtained, a turbidimetric method for the titration of Co by dithio-oxamide has been worked out. *Procedure*—To a photometer tube add successively 1 ml of 0·1 M aq. NH_3, 2 ml of 0·5% gum acacia soln. (as stabiliser), enough water to give a total volume of 50 ml (after the addition of 0·00385 M dithio-oxamide in ethanol) and titrate with cobalt soln. (≃ 0·005 M). The end-point is found graphically. With a reversed order of titration, the light absorption changes slightly with time and the determination of the end-point becomes more difficult. W. ROUBO

3266. **The rapid complexometric determination of the cobalt content of hard metals.** E. Lassner and R. Scharf (Metallwerk Plansee A.-G., Reutte, Austria). *Planseeber. Pulvermet.*, 1959, **7** (3), 129–131.—Interference in the determination of Co with EDTA by W, Nb, Ta, Ti and traces of Fe is prevented by the addition of F^- and tartaric acid; Ni and V should be absent. *Procedure*—Dissolve 0·5 g of sample, containing 4 to 20% of Co, in HF and HNO_3, add H_2O (50 ml) and tartaric acid (5 g) and make the soln. ammoniacal; adjust the total vol. to 250 ml. Take 50 ml and adjust the pH to 4 with acetic acid. Add a known excess of 0·05 M EDTA, a little ascorbic acid, 50 ml of methanol, 5 to 8 drops of PAN indicator (0·1% soln. in ethanol) and 1 g of NH_4F. Warm to 70°, titrate with 0·05 M $CuSO_4$ from a semi-micro burette to a reddish-violet, and restore the yellow colour with EDTA soln. The deviations from the mean of parallel determinations are ± 0·3% relative. P. D. PARR-RICHARD

3267. **Gravimetric determination of cobalt and nickel, and their separations from copper with N-benzoyl-N-phenylhydroxylamine.** S. K. Sinha and S. C. Shome (Presidency Coll., Calcutta,

India). *Anal. Chim. Acta*, 1959, **21** (5), 459–462.—The procedures are based on the quant. pptn. of Co or Ni at pH 6, and of Cu at pH 4, with N-benzoyl-N-phenylhydroxylamine (0·25 to 0·3 g in 10 to 15 ml of methanol). The metal complexes have the formula $M(C_{13}H_{10}O_2N)_2$ and can be weighed directly. *Procedure for Co or Ni*—Dilute the sample soln. to 300 ml (if Cl is present add 10 ml of 2% hydroxyammonium chloride soln.), heat to boiling and add slowly the reagent soln. (10 to 15 ml) after adjusting the pH to between 5·5 and 6·5 with 10% aq. Na acetate. Set the mixture aside for ≃ 1 hr., stirring occasionally, then collect and wash the ppt. and dry at 110° to 120° to const. wt. *Procedure for separating Ni or Co from Cu*—Adjust the pH of the diluted sample soln. to ≃ 4·0 with 1·5 *N* H_2SO_4 and 10% aq. Na acetate and precipitate the Cu at ≃ 100° with the reagent as described above. The filtrate can be evaporated to ≃ 300 ml and Co or Ni determined similarly therein. The error is generally ≃ ± 0·001 g for ≃ 0·03 g of metal. W. J. Baker

3268. **Estimation of nickel and palladium by α β-dioximinobutyro-o-toluidide.** J. S. Dave and A. M. Talati (Fac. of Sci., M. S. Univ. of Baroda). *J. Indian Chem. Soc.*, 1959, **36** (10), 735–738.—α β-Dioximinobutyro-*o*-toluidide quant. precipitates Ni and Pd as $M(C_{22}H_{24}O_4N_8)$, the former at pH 5·1 to 9·1 and the latter at pH 0·1 to 10·0. There is no interference from Mg^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+}, Ca^{2+}, Sr^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}, NO_3^-, Br^- or I^- in the determination of Ni, and Sn^{2+}, Hg^{2+}, Sb^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Cr^{3+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, Br^- and I^- do not interfere in the determination of Pd, but NO_3^- interfere slightly. I. Jones

3269. **Determination of calcium and magnesium in nickel and nickel alloys.** A. S. Andreev, A. N. Novikov and F. Chernÿ. *Trudÿ Leningr. Politekh. Inst.*, 1959, (201), 46–50; *Ref. Zhur., Khim.*, 1960, (3), Abstr. No. 8846.—Phosphate and pyridine-thiocyanate methods are used to remove the main components of nickel alloys; the phosphate method is recommended for all nickel-chromium alloys, including those with small Ca and Mg contents. *Procedure*—Dissolve the sample (2 to 10 g) in aqua regia, allow the soln. to evaporate at room temp., moisten the residue with HCl, add H_2O and dissolve by heating; filter off the SiO_2 - H_2WO_4 mixture. If large amounts of Fe and Al are present, remove them by pptn. as hydroxides with hexamine in a weakly acid medium; 40% formaldehyde soln. (5 to 10 ml) with an excess of aq. NH_3 soln. can also be used; Mg is not co-pptd. under these conditions, but it is possible to co-precipitate Ca and Mg with the $Cr(OH)_3$ ppt. if a considerable quantity of Cr is present. After filtration, precipitate Ca and Mg by the usual phosphate method. Wash the residue first with 5% $(NH_4)_2HPO_4$ soln. in 5% aq. NH_3 soln. and then with ethanol - amyl alcohol - H_2O (6:1:3) (100 ml) to which conc. NaOH soln. (1 drop) has been added, and finally dissolve the ppt. in HCl. Recover Mn from the soln. by a double pptn. with aq. NH_3 soln. containing Br or $(NH_4)_2S_2O_8$ and precipitate Ni with dimethylglyoxime in weakly ammoniacal medium. Remove the nickel complex with $CHCl_3$ and determine Mg and Ca in the remaining soln. The more rapid pyridine - thiocyanate method is based on the removal of interfering cations, Cu, Mn and Ni as complexes, and Al and Cr as basic salts. Filter off the SiO_2 and neutralise the filtrate with Na_2CO_3, boil to drive off CO_2, cool, add 20% KSCN soln. (20 ml) and an excess of 20% pyridine soln. Set the mixture aside for 30 min., filter off the ppt. and wash with a soln. containing pyridine (80 ml) and KSCN (20 g). With small amounts of Al and Cr remove the pyridine - thiocyanate complexes with $CHCl_3$ instead of by filtering. The second method is used for nickel - chromium samples (< 1 g). After removal of the interfering cations determine Mg photometrically with Titan yellow, adding sucrose to eliminate interference by Ca and hydroxyammonium chloride to stabilise the dye. Calculate the Ca content by difference after titration of the Ca plus Mg with EDTA soln. K. R. C.

3270. **1-(2-Pyridylazo)-2-naphthol (PAN) as a photometric reagent. Determination of zinc and cadmium in nickel.** W. Berger and H. Elvers (Entwicklungslab. der Valvo G.m.b.H. Radioröhrenfabrik, Hamburg). *Z. anal. Chem.*, 1959, **171** (4), 255–261 (in German).—PAN forms complexes with Zn and Cd which can be extracted with $CHCl_3$; Ni, Cu, Co, Mn and Fe interfere; these (except Mn) are masked by addition of KCN; Mn is removed as the PAN complex by shaking with $CHCl_3$; Zn and Cd are then freed by adding formaldehyde. *Procedure in absence of Mn*—To the weakly acid sample soln. add 2 ml of buffer soln. (70 ml of 25% aq. NH_3 and 10 g of NH_4Cl in 1 litre of H_2O) and dilute to 15 ml. Add 5 ml of 0·2 *N* KCN, 1 ml of PAN soln. (0·1% in ethanol) and 0·2 ml of 20% (by wt.) formaldehyde soln., then shake for 30 sec. and extract with 10 ml of $CHCl_3$. Measure the extinction at 520 to 540 mμ *vs.* a reagent blank. Then, if both Zn and Cd are present, shake with 10 ml of Na diethyldithiocarbamate soln. (0·225%) and measure the extinction for Zn alone. For Ni to Zn ratios of > 20:1, some Ni will be co-extracted, but can be removed by shaking the $CHCl_3$ extract with 0·02 *N* H_2SO_4, when Zn and Cd pass into the aq. phase. The method is suitable for determining microgram amounts of Zn and Cd. P. D. Parr-Richard

3271. **Analysis of nickel electrolyte [for boric acid] by means of static ion-exchange chromatography.** A. I. Lazarev and V. I. Lazareva (Akmolinsk Agric. Inst.). *Zavod. Lab.*, 1959, **25** (11), 1301.—The sample (3 to 5 ml) containing ≯ 100 mg of Ni is diluted with 20 ml of water and made just alkaline to methyl red by addition of 2% NaOH soln. Then 5 g of air-dry cationite KB-4p is introduced, the soln. is diluted to 100 ml and shaken for 10 min., and a filtered aliquot is titrated for boric acid in the presence of mannitol. G. S. Smith

3272. **Complexometric determination of nickel and magnesium in nickel-plating electrolytes.** I. M. Yurist and P. G. Shakhova. *Zavod. Lab.*, 1959, **25** (11), 1298–1299.—The electrolyte (10 ml) diluted ten times is acidified with 10% H_2SO_4, then mixed with 20 ml of 10% ammonium acetate soln., 20 ml of 0·1 *N* EDTA (disodium salt) and 5 drops of 20% sulphosalicylic acid soln., and titrated with 0·1 *N* $FeCl_3$ to give the amount of EDTA equivalent to the Ni present. The sum of Ni and Mg is determined by diluting 10 ml of the diluted electrolyte with 100 ml of water, adding 10 ml of a buffer soln. (containing 20 g of NH_4Cl and 80 ml of 25% aq. NH_3 per litre), with murexide and Eriochrome black T as indicator, and titrating with 0·1 *N* EDTA (disodium salt). G. S. Smith

3273. **Spectrophotometric determination of palladium with quinoxaline-2:3-dithiol.** G. H. Ayres and H. F. Janota (Dept. of Chem., Univ. of Texas, Austin, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1985–1987.—The method described is suitable for determining Pd in the concn. range 0·4 to 3 p.p.m. and depends on the formation of a coloured complex with the reagent in dimethylformamide soln. in the presence of a small amount of HCl. The complex has a max. extinction at 548 mμ, and the colour develops rapidly and is stable for several hours. Platinum, Os, Fe^{III}, Co and Ni interfere and must be separated from the Pd. The results on 40 samples showed an average specific extinction of 0·306 ± 0·003 per p.p.m. per cm, with a standard deviation of ± 0·004. K. A. PROCTOR

3274. **Increase of the sensitivity of spectrographic analysis of minerals by chemico-thermal concentration of the elements.** E. A. Sergeev, L. S. Margolin, P. A. Stepanov, M. V. Belobragina and N. A. Zhukova (All-Union Sci. Res. Inst. of Methods and Technique of Prospecting). *Zavod. Lab.*, 1959, **25** (12), 1455–1457.—The sample is placed in a tubular carbon electrode, which serves also as a resistor, and is heated by a current of 300 amp. so that the outside attains a temp. of 1200°. The spectrum is excited by a 10-amp. arc for about 1 min. In an alternative method, condensation of the evaporated material is used. A carrier is added to give a co-distillate. G. S. SMITH

3275. **Quantitative spectrographic analysis of ores with the introduction of the samples into the arc by means of an air stream.** Ya. D. Raikhbaum and M. A. Luzhnova (Irkutsk State Sci. Res. Inst. of Rare Metals). *Zavod. Lab.*, 1959, **25** (12), 1449–1453.—The degree of evaporation of a powdered material in an arc depends greatly on the original size of the particles and agrees approximately with a theoretical equation, the derivation of which is given. Neglect of standardisation of the particle size when the elements to be determined are not highly volatile leads to errors. With Zr, the intensities of the lines of 300-mesh material are four times those of 200-mesh material.

G. S. SMITH

3276. **Pyrohydrolysis of cryolite and other fluoride-bearing materials.** H. P. Silverman and F. J. Bowen (Kaiser Aluminum and Chemical Corp., Pennanente, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1960–1965.—An apparatus and procedure for the quant. pyrohydrolysis, by reaction with steam for ≮ 15 min. at 1200° ± 50°, of AlF_3, cryolite and reduction-cell electrolytes are described. The need for a separate steam-preheater is obviated by use of a nickel reactor (24 in. by 1 in.) which can be inserted in the tube-furnace. The total condensate collected is titrated, preferably with 0·2 *N* NaOH, with phenolphthalein as indicator, first at room temp. and then to the final end-point at or near boiling. The sample of cryolite (100 mesh, 0·25 g) is mixed with α-Al_2O_3 (0·75 g) as accelerator; layers of α-Al_2O_3 (1 g in all) are placed above and below the mixture in the nickel combustion-boat. No accelerator is required for AlF_3. The recovery of F^- is ≃ 99% and the standard deviation is 0·27% (47 analyses). The fluoride value found should be multiplied by a recovery factor of 1·006 (for cryolite) and 1·010 (for AlF_3). The procedure can be applied to the analysis of other fluorides; Cl^- and SO_4^{2-} interfere in the pyrohydrolysis of AlF_3 and, although CaF_2 is not completely hydrolysed, its concn. (≃ 8%) in a reduction-cell electrolyte does not cause any large error in the total F^- as determined by this method. W. J. BAKER

3277. **Decomposition of chrome-magnesite by means of sintering.** Yu. I. Usatenko and E. A. Klimkovich (F. E. Dzerzhinskii Dniepropetrovsk Chem.-Tech. Inst.). *Zavod. Lab.*, 1959, **25** (11), 1295–1296.—Decomposition is carried out by heating the material (0·5 g) with anhydrous Na_2CO_3 (0·4 g) for 10 min. at 1000°. G. S. SMITH

3278. **Infra-red spectroscopy as a method for the determination of mineralogical constitution of ceramic raw materials and products.** H. Lehmann and H. Dutz. *TonindustrZtg*, 1959, **83**, 219.—Infra-red spectra of 70 silicates at wavelengths between 1300 and 417 cm^{-1} were measured. For most of these minerals, the spectra between 667 and 417 cm^{-1} had not previously been determined. The compositions of 5 two-component clay-mineral systems were determined by this technique to within ± 3%, which is equal to the accuracy of X-ray analysis. The much discussed displacement of SiO oscillations towards higher valencies with increasing linkage of the SiO_4 tetrahedra is interpreted on the basis of an increase of the force constants. ABSTR. BRIT. CERAM. SOC.

3279. **Rapid analysis of Talbot-steel slags.** F. Eliáš (VŽKG, Ostrava, Czechoslovakia). *Hutn. Listy*, 1959, **14** (11), 1009–1010.—The sample is dissolved in a mixture of HF and $HClO_4$ and aliquots of soln. are used for the determination of FeO, MnO, P_2O_5 and CaO. A separately prepared soln. is recommended for the determination of SiO_2. *Procedure*—Dissolve the sample (0·5 g) in $HClO_4$ (70%) (15 ml) and evaporate the acid. Cool, carefully add gelatin soln. (1%) (15 ml), heat, filter, and wash the ppt. Then ignite the filter with the ppt. at 1000° and weigh as SiO_2. To another portion of sample (0·5 g) in a platinum dish add HF (3 ml) and heat, then add $HClO_4$ (70%) (10 to 15 ml) and heat for 10 min. Cool the product and make up to 500 ml with H_2O. Determine CaO volumetrically on a 100-ml aliquot after separation of the oxalate. For FeO, to a second aliquot (50 ml) add hot H_2O (50 ml), salicylic acid as indicator (2% soln. in ethanol) (3 ml), adjust to pH 2 to 3 with ammonium acetate soln. (5%) and titrate at 60° with 0·01 *M* EDTA (disodium salt). Determine MnO by titrating a 20-ml aliquot (oxidised by persulphate) with sodium arsenite soln. For P_2O_5, to a fourth aliquot (5 ml) add ammonium molybdate soln. (dissolve 25 g of ammonium molybdate in 300 ml of H_2O, add 20 ml of H_2O and 200 ml of dil. H_2SO_4) (2 ml), quinol soln. (0·5%) (5 ml) and Na_2SO_4 soln. (20%) (5 ml), and set aside for exactly 5 min. Dilute to 100 ml, mix, and measure the extinction spectrophotometrically with the use of a yellow filter. J. ZÝKA

See also Abstracts—**3015**, Automation in steel analysis. **3110**, Tri-*n*-octylphosphine oxide as extraction solvent. **3114**, Investigations with PAN. **3282**, Reactivity of oxidising agents with KI. **3367**, Detection of nitrogen oxides in coke-oven gas. **3384**, Zinc and ZnO in lithopone. **3563**, Sampling ferrous metals. **3583**, Moisture in gases.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives, etc.

3280. **Polarographic analysis in organic chemistry.** M. P. Souchay (Fac. des Sci., Paris, France). *Chim. Anal.*, 1959, **41** (11), 445–455; (12), 471–476.—A general review is presented of the theory and practice of classical polarographic methods as applied to organic compounds, with special reference to (*i*) relations between $E_{\frac{1}{2}}$ and mol. structure, (*ii*) determination of trace amounts, including non-reducible substances (*e.g.*, mono- and di-methylamines in the presence of trimethylamine and ammonia), (*iii*) the elucidation of reaction mechanisms, and (*iv*) polarography in non-aq. media.
W. J. BAKER

3281. **Photometric titration of weak bases in non-aqueous media.** L. E. I. Hummelstedt and D. N. Hume (M.I.T., Cambridge, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. AECU-4561, 1959, 31 pp.—The photometric titration technique is used for the determination of weak bases, with $HClO_4$ in acetic acid as titrant and acetic acid or methyl cyanide as solvent. Differential titration of as many as four components in a single mixture is shown to be possible. Comparison with potentiometric titrations in the same media shows the photometric technique to be preferable in many cases where the bases to be differentiated are very similar in strength. The versatility of the photometric procedues in differentiating bases is greatly increased by the device of changing wavelength during titration of mixtures. NUCL. SCI. ABSTR.

3282. **Reactivity of oxidising agents with potassium iodide reagent.** A. P. Altshuller, C. M. Schwab and M. Bare (R. A. Taft San. Engng Center, U.S. Dept. of Health, Cincinnati, Ohio). *Anal. Chem.*, 1959, **31** (12), 1987–1990.—The reactivity of 6×10^{-2} *M* I^- with O_2, H_2O_2, NO_2^-, peracetic acid, succinic acid peroxide, cumene hydroperoxide, di-*tert.*-butyl peroxide and *tert.*-butyl nitrite (all in concn. of 10^{-4} to 10^{-5} *M*) was followed spectrophotometrically at pH values from 1 to 14. For the lower values the soln. were acidified with H_3PO_4 (3·6 or 36%) saturated with sulphamic acid (to evaluate its effect in quenching the reaction between I^- and NO_2^-). The reaction-rate curves are discussed in respect of the optimum conditions under which determinations of oxidising materials in the atmosphere would be least dependent on time of keeping the soln. before measuring the extinction.
W. J. BAKER

3283. **Continuous coulometric determination of parts per million of moisture in organic liquids.** L. G. Cole, M. Czuha, R. W. Mosley and D. T. Sawyer (Consolidated Electrodynamics Corp., Pasadena, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2048–2050.—The instrument comprises a high-efficiency stripping column in which the H_2O from a continuously flowing sample stream is quant. removed by a countercurrent stream of dry N. The gas is then passed through a coulometric cell consisting of anhydrous P_2O_5 between platinum electrodes. Good agreement with the results obtained by the Karl Fischer method was attained, and accurate analysis can be carried out at the 1 p.p.m. level. G. P. COOK

3284. **Use of the alkaline-earth metals for the detection and determination of elements in organic substances.** A. P. Terent'ev, P. N. Fedoseev and N. P. Ivashova. *Izv. Vyssh. Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, 1959, **2** (1), 54–58; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,370.—Methods for the determination of N, S and halogens in organic substances after their decomposition with metallic magnesium or calcium and for the detection of C, N, S and halides by using metallic calcium have been developed. *Qualitative analysis*—Mix 1 to 5 mg of an organic substance with 60 to 70 mg of magnesium powder or 90 to 116 mg of calcium in a glass tube (*A*), close it with a gas-delivery tube (*B*) with its end immersed in water and when determining N displace air by diethyl ether from the tubes (*A*) and (*B*). When using calcium absorb the air by metallic calcium heated at 700° to 800° placed in a quartz or porcelain tube (*C*) fitted to the tube (*A*). Heat the tube (*A*) to redness, then cool and transfer the contents to a dry test-tube and treat with water to dissolve nitrides, sulphides and halides of Mg (Ca). The elements (N, S, halogens) are then detected by the conventional methods: S with sodium nitroprusside or Pb acetate, N with Nessler reagent, and halogens by $AgNO_3$. To detect C, treat the CaC_2 formed with acetic acid and detect the resulting acetylene with Ilosvay reagent. *Quantitative determination*—Mix the organic sample (0·050 to 0·070 g) with 50 to 100 mg of magnesium (calcium), add an excess (1 to 2 g) of the metal and then proceed as described above. Determine S iodimetrically after removing H_2S from the acidified soln. and absorbing it in Zn or Cd acetate. Make the soln. alkaline and determine N as NH_4^+ by titration. Finally determine the halogen by $AgNO_3$ titration.
W. ROUBO

3285. **Rapid determination of nitrogen in organic substances.** Kusuo Narita and Masako Ishii (Pharm. Inst., Med. Fac., Hokkaido Univ., Sapporo). *J. Pharm. Soc. Japan*, 1959, **79** (4), 407–410.—The use of MnO_2 as an auxiliary combustion agent for the determination of N by the Dumas micro-method was examined. A sample is weighed into a platinum boat, covered with $\simeq$ 50 mg of MnO_2 (White *et al.*, *Anal. Chem.*, 1958, **30**, 409) and put on a magnetic boat-carrier. The carrier is inserted into a combustion tube and the air is replaced by a rapid current of CO_2 for 15 sec. by a half-way flash-back system. The combustion tube is connected to two nitrometers by a four-way stopcock, which makes two determinations possible. Combustion is completed after 10 min., when the temp. of the movable furnace of the combustion tube reaches 950°, and N gas is expelled 5 min. later. These improvements make possible continuous operation of 3 or 4 runs per hr. S. NATORI

3286. **Rapid method for the micro-determination of halogen in organic compounds.** F. W. Cheng (Chem. Res. Dept., Atlas Powder Co., Wilmington, Delaware, U.S.A.). *Microchem. J.*, 1959, **3** (4), 537–542.—After combustion of the sample, the halide ion is determined by titration with $Hg(NO_3)_2$ soln., with diphenylcarbazone as indicator. Dissociation of the mercuric halide is suppressed and the quality of the end-point is improved by the addition of ethanol. *Procedure*—Burn the sample containing 1 to 1·5 mg of halogen in a 300-ml oxygen flask

containing 0·5 *N* KOH (1 ml) and 6% H_2O_2 soln. (15 ml). Shake and set aside for 30 min. Add 10 ml of water and boil for 5 min. to destroy H_2O_2. Cool, add ethanol (100 ml) and neutralise to bromophenol blue with HNO_3 (0·5 and 0·05 *N*), adding 1 ml of 0·05 *N* HNO_3 in excess. Add 0·5% ethanolic diphenylcarbazone soln. (15 drops) and titrate with 0·02 *N* $Hg(NO_3)_2$. The method is accurate to within ± 0·3%, and can be applied to compounds containing S and N.

W. T. CARTER

3287. **Sub-micro methods for the analysis of organic compounds. X. Determination of fluorine.** R. Belcher, M. A. Leonard and T. S. West (The Univ., Birmingham, England). *J. Chem. Soc.*, 1959, 3577–3579.—Fluorine (10 to 40 μg) is determined by combustion in an oxygen-filled flask and the fluoride produced is determined by the blue colour formed with the Ce^{III} - alizarin complexone complex. Other halides, sulphate or nitrate do not interfere. Phosphate and arsenate have little effect in concn. similar to that of the fluoride. *Procedure*—Samples are dried over P_2O_5 and folded in filter-paper which is held in a platinum wire attached to a ground glass stopper. The paper is lighted and burned off in a 250-ml conical flask containing 30 ml of water and an atmosphere of oxygen. The resulting soln. of the gases formed is added to 10 ml of 0·0005 *M* alizarin complexone (1:2-dihydroxyanthraquinon-3-ylmethylamine-NN-diacetic acid) in a 100-ml flask. Acetate buffer (2 ml) (to give pH 4·3) is added and the soln. is diluted to ≃ 75 ml, then 10 ml of 0·0005 *M* $Ce(NO_3)_3$ is added and the soln. is made up to 100 ml. After 1 hr. with the soln. protected from light and draughts the extinction is measured at 610 mμ. The calibration curve is prepared with standard soln. of NaF. If $-CF_3$ groups are present in the sample, it is covered with 1 mg of $KClO_3$ before ignition. An accuracy within ± 0·5% is achieved.

E. J. H. BIRCH

3288. **Micro-determination of fluorine in organic compounds following a modified Schöniger combustion.** A. Steyermark, R. R. Kaup, D. A. Petras and E. A. Bass (Hoffman-La Roche Inc., Nutley, N.J., U.S.A.). *Microchem. J.*, 1959, **3** (4), 523–527.—The method is essentially that of Senkowski *et al.* (*Anal. Abstr.*, 1960, **7**, 1774), with the sample size reduced to < 10 mg. The sample is burnt in an oxygen-filled flask after the addition of 15 to 20 mg of Na_2O_2, the combustion products are absorbed in water, and the F^- are titrated photometrically with 0·01 *N* $Th(NO_3)_4$ at pH 3·0, with Na alizarinsulphonate as indicator. Nitrogen, S and halogens do not interfere but, if the sample contains Hg, P or As, F^- are steam-distilled as H_2SiF_6 from $HClO_4$ before titration. The analysis of a wide range of organic substances containing fluorine gave standard deviations between 0·05 and 0·36%.

W. T. CARTER

3289. **Determination of fluorine in phosphoro- and phosphono-fluoridates.** S. Sass, N. Beitsch and C. U. Morgan (Chem. Warfare Lab., Army Chemical Center, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1970–1974.—The procedures described, which are applicable to samples of DFP (di*iso*propyl phosphonofluoridate) and Sarin (*iso*propyl methylphosphonofluoridate) and to mixtures of ester phosphorus monofluoridate (**I**), difluoridate (**II**) and HF, obviate the distillation of F from the residue of hydrolysed phosphate before titration and also permit ionic F and hydrolysable F (*viz*, one F atom in the mol. of **II**) to be determined without hydrolysis. *Determination of total F*—The sample of fluoridate (containing ≯ 15 mg of F) is hydrolysed with 0·05 *M* ethanolic Na ethoxide at 25° (under reflux if necessary) and the total F^- in the soln. is then titrated directly at pH 3 with standard $Th(NO_3)_4$ soln., with alizarin red S as indicator. The esterified P does not interfere, and the accuracy is high. *Determination of ionic and hydrolysable F*—(*i*) Because of the hydrolytic stability of some fluoridates in H_2O at pH 3, the combined F^- in **I** and the hydrolysable F in **II** can be determined (to within 0·5%) in **I** and **II**, or mixtures thereof, by direct titration at 25° with Th - alizarin red S. The content of HF in **II** is calculated as the difference between one-half the total F^- and the value of the combined ionic and hydrolysable F titrated together. (*ii*) For a sample of **II** alone (0·3 to 0·4 g), the F^- are first determined by titration at ≃ 0° with 0·1 *N* NaOH, with methyl red - bromocresol green (pH 5·1) as mixed indicator. The hydrolysable F is then determined, on a fresh sample, by titration with ethanolic 0·1 *N* tributylamine, with bromocresol green as indicator (only the acids are titrated so that the content of **II** in the sample can be calculated from the difference between the aq. and non-aq. titrations). The content of HF can then be obtained, by difference, from the determination of F^-. The results listed for 10 different compounds show high reproducibility and accuracy.

W. J. BAKER

3290. **Spectrophotometric method for the determination of chlorine in organic compounds. A semi-micro and micro-method.** I. Lysyj (Food Machinery and Chem. Corp., Control Res. Lab., Princeton, N.J., U.S.A.). *Microchem. J.*, 1959, **3** (4), 529–536.—After combustion of the sample, Cl^- are determined by metathesis with mercuric chloranilate (**I**), the chloranilic acid liberated being determined spectrophotometrically. For large amounts of Cl^- (0·25 to 12 mg), the absorption peak at 530 mμ is used but, for smaller amounts (0·025 to 0·25 mg), the more intense absorption peak at 305 mμ is more suitable. *Procedure*—Burn the sample (≯ 25 mg) in a Schöniger oxygen flask containing 6% H_2O_2 soln. (25 ml) and 6% aq. NH_3 (25 ml). Evaporate the soln. to 10 ml, add 2-methoxyethanol (50 ml), *N* HNO_3 (5 ml) and 0·3 g of **I** and dilute the soln. to 100 ml. Shake for 10 min., then filter, and after 15 min. measure the extinction against a blank at 530 or 305 mμ. Sulphur, P and N do not interfere. For a series of compounds containing 17 to 62% of Cl, the average recovery was 99·4%, and the standard deviation 0·75%, but for small amounts of Cl the method was much less accurate.

W. T. CARTER

3291. **The flask combustion technique in pharmaceutical analysis: iodine-containing substances.** C. A. Johnson and C. Vickers (Anal. Development Group, Standards Dept., Boots Pure Drug Co. Ltd., Nottingham, England). *J. Pharm. Pharmacol.*, 1959, **11** (Suppl.), 218T–222T.—The flask method for the combustion of organic samples (*cf.* Schöniger, *Anal. Abstr.*, 1955, **2**, 1816) has been applied to a number of iodine-containing substances of pharmaceutical interest, including the non-staining iodine ointments. The method is rapid and simple and only small samples (*e.g.*, 10 to 25 mg) are used. The accuracy and precision of the results attained show that it is suitable for routine control use.

A. R. ROGERS

3292. **Determination of sulphur-35 in organic substances.** A. Habersbergerová-Jeníčková and J. Cífka (Inst. Nucl. Res., Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3777–3782 (in German).—The sample is burnt in O by the method of Schöniger (*Mikrochim. Acta*, 1956, 869) and the sulphate is pptd. with $Ba(ClO_4)_2$. The method of combustion in a quartz tube and absorption of sulphate on silver gauze is less satisfactory. *Procedure*—To the soln. of the burnt sample (10 to 25 mg) add $HClO_4$ to 0·1 *M* concn. and evaporate to 10 ml. Wash the combustion flask with H_2O (50 ml), evaporate the combined soln. and washings, heat to 95° and add 0·02 *M* $Ba(ClO_4)_2$ (10 ml) at the same temp.; mix for 3 min., cool and filter after 1 hr. Wash the ppt. with H_2O (100 ml). Ignite the $BaSO_4$ for 40 min. at 650° and measure the activity. The content of ^{35}S was determined in Tropaeolin OO (C.I. Acid Orange 5), sulphanilamide, 1-naphthylamine-4-sulphonic acid, N-acetylsulphanilic acid, phenothiazine, sulphanilic acid and methionine, with an average error $\gtrsim \pm$ 0·30%. The preparation of the labelled compounds is described. J. ŽÝKA

3293. **The complexometric finish to the determination of sulphur in organic substances after different methods of decomposition.** U. Bartels and H. Hoyme (Inst. f. Faserstoff-Forsch., Teltow-Seehof, Germany). *Chem. Tech., Berlin*, 1959, **11** (11), 600–603.—For the routine determination of S, the sample is best burnt in O by the method of Schöniger (*Mikrochim. Acta*, 1956, 869); the H_2SO_4 produced is determined by adding an excess of $BaCl_2$ and back-titrating the excess with EDTA. The method is rapid and accurate for S contents of $\lesssim$ 0·2%. Other possible methods of decomposition (*e.g.*, reduction to H_2S with $SnCl_2$ or oxidation with Na_2O_2) have disadvantages and the Carius procedure with fuming HNO_3 is unsuitable for complexometry. J. P. STERN

3294. **Determination of arsenic in organic compounds. Rapid micro- and semi-micro methods.** M. M. Tuckerman, J. H. Hodecker, B. C. Southworth and K. D. Fleischer (Temple Univ., School of Pharmacy, Philadelphia, Pa., U.S.A.). *Anal. Chim. Acta*, 1959, **21** (5), 463–467.—In the procedures given, 28% $HClO_3$ soln. is used for the digestion of the sample (0·25 to 5 mg) at 180°; the excess of $HClO_3$ is boiled off leaving a $HClO_4$ soln. of the inorganic elements in their higher oxidation states. There is no loss of As even when 4 *M* chloride is present. In the semi-micro method the As^{5+} in the neutralised digest are reduced with HI, the liberated iodine is removed with $Na_2S_2O_3$ and the As^{3+} are titrated with 0·005 *N* iodine in a soln. saturated with $NaHCO_3$. The error varies from −0·5 to + 2·2%; Bi interferes. In the micro-method the neutralised digest is diluted to 100 ml, and the As in a 2-ml aliquot is determined colorimetrically at 660 mμ as a heteropoly molybdenum blue, a single reagent soln. (ammonium molybdate - basic bismuth carbonate - H_2SO_4 - ascorbic acid being used at 25°. Beer's law is followed by $\gtrsim$ 40 μg of As in 10 ml; the colour is stable and reproducible, so that only one calibration curve for the instrument is required. The error varies from −0·6 to + 5·3%; P interferes and should be removed, after digestion of the sample with $HClO_3$, by the method of Jean (*cf. Anal. Abstr.*, 1956, **3**, 2050). W. J. BAKER

3295. **Solid scrubbers in the Zeisel alkoxyl determination.** D. M. W. Anderson and J. L. Duncan (Dept. of Chem., Edinburgh Univ., Scotland). *Chem. & Ind.*, 1959, (37), 1151–1152.—Good results for all C_1 to C_4 alkoxyl groups have been obtained (with and without added inorganic sulphate) with soda asbestos as scrubber. This completely absorbs H_2S, HI, CO_2 and iodine, but does not retain alkyl iodides. E. G. CUMMINS

3296. **Determination of the *iso*cyanate and *iso*thiocyanate groups. Micro- and semi-micro methods.** B. S. Karten and T. S. Ma (Dept. of Chem., Brooklyn Coll., New York, U.S.A.). *Microchem. J.*, 1959, **3** (4), 507–514.—The method of Siggia and Hanna (*cf. Anal. Chem.*, 1948, **20**, 1084) is adapted to the micro- and semi-micro scale. The *iso*cyanates and *iso*thiocyanates react with excess of *n*-butylamine in dioxan soln. to form substituted ureas and thioureas, respectively. The excess of *n*-butylamine is determined by back-titration with standard acid. Results are quoted for seven aromatic *iso*cyanates, one aromatic di*iso*cyanate, and five aliphatic and two aromatic *iso*thiocyanates. The precision is ± 0·5% and, unlike the macro-method, heating is unnecessary to complete the reaction. W. T. CARTER

3297. **Catalyst for the determination of methane in the atmosphere of mines.** V. S. Kravchenko, I. E. Birenberg, E. F. Karpov and I. A. Magidson (Mining Inst., Acad. Sci., USSR). *Zavod. Lab.*, 1959, **25** (12), 1448.—For intense flameless combustion of methane at 360°, active Al_2O_3, on which are deposited Pt and Pd, is recommended as a catalyst. G. S. SMITH

3298. **Separation of C_4 and lighter hydrocarbons by gas - liquid chromatography.** T. A. McKenna, jun., and J. A. Idleman (Firestone Synthetic Rubber and Latex Co., Orange, Tex., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2000–2003.—A 50-ft. column of a mixture of glutaronitrile and propylene carbonate in a ratio of 3 to 7, at a concn. of 23% by weight on 40 to 50-mesh Chromosorb, operating at room temp., gave the best resolution for the C_1 to C_4 hydrocarbons, with He as the carrier gas. Such a column can be used continuously for many months without deterioration. Washing of the Chromosorb with acid produces no noticeable improvement in column efficiency. K. A. PROCTOR

3299. **Interaction of β-particles with matter. Analysis of hydrocarbons by β-ray backscattering.** P. R. Gray, D. H. Clarey and W. H. Beamer (Radiochemistry Lab., The Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2065–2068.—A rapid, simple, accurate and non-destructive determination of C to H ratios of hydrocarbons is described. Mass density has a small effect on the β-ray backscatter intensity, and the sample density must be known to 0·01 g per ml. The standard deviation of the carbon content (%) in 13 hydrocarbons was $<$ 0·03, and both mixtures of liquid hydrocarbons and soln. of solid hydrocarbons in hydrocarbon solvents can be analysed with this precision. K. A. PROCTOR

3300. **Analysis of isoprene by gas chromatography.** F. Armitage (Res. and Development Div., Polymer Corp. Ltd., Sarnia, Ontario, Canada). *J. Chromatography*, 1959, **2** (6), 655–657 (in English).—Retention data are listed for 28 hydrocarbons, some

of them commonly associated with isoprene, eluted from dimethyl sulpholane on Johns Manville Chromosorb and from benzyl cyanide - $AgNO_3$ on the same adsorbent. G. S. ROBERTS

3301. **The reaction of bases with chloroform.** D. I. Coomber and B. A. Rose (Lab. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *J. Pharm. Pharmacol.*, 1959, **11** (11), 703–704.—A number of samples of chloroform manufactured before 1941 were found to be free from dichloromethane and bromochloromethane and they failed to react with strychnine on boiling for 9 hr. (*cf.* Caws and Foster, *Anal. Abstr.*, 1957, **4**, 648; 1958, **5**, 2760). Strychnine does not react with chloroform made by the bleaching powder process, even when bromine is present in appreciable quantities in the bleaching powder, and chloroform made in this way is likely to be the best material for use in the analysis of organic bases. A. R. ROGERS

3302. **Determination of hydroxyl value of alcohols by near-infra-red spectroscopy.** R. O. Crisler and A. M. Burrill (Miami Valley Lab., The Procter & Gamble Co., Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2055–2057.—The method described, in which the samples are examined as dil. soln. in CCl_4 or tetrachloroethylene, is based on the use of the OH-stretching overtone band at 1·4 μ. The results on a number of fatty alcohol samples have been compared with the values obtained by the acetic anhydride - pyridine method, and the standard deviation is 0·27 in the range 85 to 115 mg of hydroxyl per g of sample. Some differentiation between types of hydroxy compounds is possible, and the method can probably be extended to other alcohols, particularly tertiary, and others difficult to acetylate.

K. A. PROCTOR

3303. **Determination of alcohols by the isotopic dilution method.** V. Ya. Efremov, M. B. Neiman and V. N. Panfilov. *Trudy Komiss. po Anal. Khim. Akad. Nauk SSSR*, 1958, **9** (12), 361–366; *Ref. Zhur., Khim.*, 1959, (12), Abstr. No. 42,152.—The method (*Ref. Zhur., Khim.*, 1957, Abstr. No. 8405) is based on the addition of a known amount (a) of radioactive alcohol, of known specific activity (α), to a mixture of products containing an unknown amount (x) of inactive alcohol. The specific activity (β) of the resulting mixture is then measured and the formula $x = a(\alpha/\beta - 1)$ is applied. The error depends on the accuracy of measurement of the indicated quantities and on the dilution (α/β). An 8- or 10-fold dilution is recommended. The separate alcohols are pptd. from the treated mixture as the 3:5-dinitrobenzoates, which are analysed radiometrically. In determining methanol and ethanol in a mixture, $^{14}CH_3OH$ and $CH_3{}^{14}CH_2OH$ were added and the alcohols were converted into the 3:5-dinitrobenzoates, which were separated chromatographically (*Ref. Zhur., Khim.*, 1957, Abstr. No. 50,751) in soln. in light petroleum on a silica gel column, eluted with a mixture of light petroleum and diethyl ether, and their specific activity measured. The maximum error is 5%. The method may be used for determining methanol in the oxidation products of propylene. C. D. KOPKIN

3304. **Mercurimetric determination of allyl alcohol.** M. Wroński (Inst. Chem. Technol., Univ. Lódź, Poland). *Z. anal. Chem.*, 1959, **171** (3), 177–178 (in German).—Allyl alcohol (**I**) reacts with Hg^{2+} to give a soluble product, but the change in concn. of Hg^{2+} can be used to measure the amount of **I**. Excess of acetone interferes, but methanol or ethanol does not. *Procedure*—(*a*) Dilute 0·5 to 50 mg of **I** with 5 to 50 ml of H_2O and add excess of $Hg(NO_3)_2$ soln. Acidify with 1 ml of *N* HNO_3 and after a few seconds dilute with H_2O to between 50 and 100 ml; add 5 ml of *N* aq. NH_3 and 1 ml of thiofluorescein soln. (0·02% in 0·1 *N* aq. NH_3). Titrate with 0·01 *N* thioglycollic acid to a blue end-point. (*b*) Titrate an aliquot of $Hg(NO_3)_2$ soln. in the same way. Then $(b - a) \times 0{\cdot}01 \times 58{\cdot}08 =$ **I** (mg). The deviation on 4 determinations of 4 mg of **I** was ± 0·2%.

P. D. PARR-RICHARD

3305. **Determination of a substituted glycol by electrolytic oxidation.** H. A. Rose (Eli Lilly & Co., Indianapolis, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2103–2104.—Phenaglycodol (2-*p*-chlorophenyl-3-methylbutane-2:3-diol) can be split by electrolytic oxidation to give a product that can be measured by u.v. absorptiometry. The recoveries were about 100% and the coeff. of variation ± 0·64% at the 300-mg level. G. P. COOK

3306. **Separation and identification of alkoxyglycerols [alkoxypropanediols].** B. Hallgren and S. O. Larsson (Dept. of Med. Biochem., Univ. of Gothenburg, Sweden). *Acta Chem. Scand.*, 1959, **13** (10), 2147–2148 (in English).—The alkoxypropanediol fractions of the liver oils of Elasmobranch fishes (*Squalus acanthias, Somniosus microcephalus* and *Chimaera monstrosa*) are obtained by adsorbing the unsaponifiable fraction on alumina, eluting the hydrocarbons with light petroleum, the cholesterol with dichloromethane and finally the alkoxypropanediols with 10% of methanol in dichloromethane. The alkoxypropanediols are converted into dimethyl ethers with diazomethane - BF_3 (Müller and Rundel, *Angew. Chem.*, 1958, **70**, 105), separated from monomethyl ethers and unchanged material by chromatography on alumina, and subjected to gas chromatography, with He as carrier gas and silicone grease and a polyester (Reoplex 400) as stationary phases. The products are condensed and identified by mass spectrometry. Compositions are reported.

E. J. H. BIRCH

3307. **Contributions to the analysis of 1:2-glycols and polyhydric compounds. III. Direct iodimetric determination of glucose by means of the aldehyde formed during oxidation with periodic acid.** L. Maros and E. Schulek (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1959, **21** (1), 91–96 (in German).—The method used for tartaric acid (*Anal. Abstr.*, 1960, **7**, 2271) has been applied to the determination of glucose; after conversion of the formaldehyde into the bisulphite compound the latter is treated with KCN, and the SO_3^{2-} so liberated are titrated with 0·1 *N* iodine (1 ml ≡ 9·008 mg of glucose). P. D. PARR-RICHARD

3308. **Condensation of saccharides with carbonyl compounds in the presence of ethyl metaphosphate.** J. Pacák and M. Černý (Dept. Org. Chem., Charles' Univ., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3804–3807 (in German).—For the detection of the *iso*propylidene derivatives of D-mannose, D-xylose, D-mannitol, D-sorbitol and dulcitol, prepared by reaction with ethyl metaphosphate and acetone, a soln. of ammonium ceric

nitrate in HNO_3 is used. The derivaties are separated by paper chromatography with *n*-butanol - ethanol - H_2O - aq. NH_3 (40:10:49:1), and the paper is sprayed with the reagent (30% of ammonium ceric nitrate in 2 *N* HNO_3) and carefully heated. White spots on a yellow background reveal the *iso*propylidene derivatives; R_F values for 1:2-O-*iso*propylidene-D-glucose and 1:2-5:6-di-O-*iso*propylidene-D-glucose were 0·74 and 0·93, respectively. J. ZÝKA

3309. **Polarographic determination of aliphatic aldehydes and ketones as imines.** M. E. Hall (Chemstrand Corp., Decatur, Ala., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2007–2009.—The carbonyl compounds are converted into imines at a pH > 12 by reaction with hexamethylenediamine (**I**) and the imino group is then reduced at the dropping mercury electrode. The excess of **I** acts as the supporting electrolyte, a 2% soln. being used for the determination of aldehydes and a 20% soln. for ketones. Aldehydes are distinguished from ketones since their corresponding imines are reduced at different voltages, the $E_{\frac{1}{2}}$ values being ≃ 1·6 and 1·8 V*vs.* the S.C.E., respectively. The average error in the 0 to 20% concn. range is 1·5%. G. P. COOK

3310. **Paper chromatography of 2:4-dinitrophenylhydrazones. Estimation of alkan-2-one, *n*-alkanal, alk-2-enal and alka-2:4-dienal derivatives.** R. Ellis and A. M. Gaddis (U.S. Dept. Agric., Beltsville, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1997–2000.—The methods of Ellis *et al.*, and Gaddis and Ellis (*cf. Anal. Abstr.*, 1958, **5**, 3020; 1959, **6**, 4817), were applied. In experiments with four mixtures the average deviation from the mean was 3·4%. G. P. COOK

3311. **Photometric determination of water in ketones, esters and ethers.** E. Jackwerth and H. Specker (Inst. für Spektrochemie u. angew. Spektroskopie, Dortmund-Aplerbeck). *Z. anal. Chem.*, 1959, **171** (4), 270–274 (in German).—The water content of ketones, esters and ethers is determined by their reaction with LiCl and $Cu(ClO_4)_2$ to give orange - red $LiCuCl_3$; the change in extinction is linear for H_2O contents of 0·1 to 5%. *Procedure*—Place a known vol. of H_2O (0·1 to 2·0 ml) in each of a series of 50-ml flasks and dilute to vol. with dry acetone. Pipette 25 ml into the titration cell, add 3 ml of 0·01 *M* LiCl in dry acetone and run in 0·001 *M* $Cu(ClO_4)_2$ in dry acetone until the max. response is reached on the photometer at 366 mμ; plot a calibration curve. Determine the H_2O content on 25 ml of test liquid in the same way. For esters and ethers use the solvent saturated with H_2O at 20° for calibration and dilute accordingly. The variance for H_2O in acetone (10 determinations) was 1·6%. Instead of titrating, the extinction can be measured directly by adding 1 ml of 0·01 *M* $Cu(ClO_4)_2$. Small amounts of aldehyde do not interfere, but lower alcohols must be absent.
P. D. PARR-RICHARD

3312. **Morphological identification of some organic acids as the sodium salts.** B. R. Havlik, L. M. Marshall and J. P. Lodge (Taft San. Engng Center, Pub. Health Service, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio). *J. Chromatography*, 1959, **2** (6), 620–625 (in English).—Crystals of characteristic appearance are produced by volatile organic acids diffusing from appropriate soln. towards NaOH pellets in a Conway cell. The method is useful for identifying an organic acid in a small vol. of a dil. soln. G. S. ROBERTS

3313. **The conductimetric titration of carboxylic and phenolic acids in non-aqueous solutions. III. The resolution of acid mixtures and some practical applications.** N. van Meurs and E. A. M. F. Dahmen (Shell Internat. Res. Maatschappij N.V., Amsterdam, Holland). *Anal. Chim. Acta*, 1959, **21** (5), 443–455.—Numerous non-aq. conductimetric titrations of ternary mixtures of acids, of two dibasic acids in non-solvating media, and of binary mixtures of carboxylic acids, or of carboxylic and phenolic acids, are reported and the optimum conditions in respect of titrant and solvent are discussed extensively. Single compounds, *e.g.*, diphenylolpropane [2:2-di-(*p*-hydroxyphenyl)propane] and perchloric acid, and mixtures (*e.g.*, naphthenic acids and inorganic acids containing H_2SO_4) can be analysed accurately, often with an error < 0·5%, under suitable conditions. In general, 0·1 to 0·3 *N* tetrabutylammonium hydroxide is the preferred titrant, although, in some instances, only alkali-metal methoxides can be used. The most favourable solvent is pyridine, but a mixture of dimethylformamide and benzene (1:3 by vol.) is satisfactory. Ternary mixtures containing a strong monobasic, a weak monobasic and a weak dibasic acid (*e.g.*, $HClO_4$ - HCl - phthalic acid) can be thus resolved conductimetrically. The procedure used has been described previously (*Anal. Abstr.*, 1960, **7**, 1419).
W. J. BAKER

3314. **Determination of organic acids in solutions of chromic acid.** H. H. Barber, jun., and W. H. Clingman, jun. (American Oil Co., Texas City, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2069–2071.—The method is based on the procedure of Bulen *et al.* (*cf. Ibid.*, 1952, **24**, 187). Chromic acid and other inorganic materials are first removed from the sample by pptn. and chromatographic techniques and the organic acids are separated chromatographically and determined by the Bulen procedure. Two chromatograms are obtained, one of the total carboxylic acids and one of the dibasic acids alone, the monobasic acids being measured by difference. Isomeric monobasic acids in the chromatographic fractions can be identified by mass spectrometry.
G. P. COOK

3315. **Organic chemical microscopy. III. *p*-Toluidides and amides as qualitative organic derivatives of carboxylic acids.** R. E. Dunbar and C. C. Moore (N. Dakota State Coll., Fargo, U.S.A.). *Microchem. J.*, 1959, **3** (4), 491–505.—Methods of preparation of the derivatives are described and photomicrographs are given of 28 *p*-toluidides and 10 amides. The use of the photographs is recommended in the identification of organic acids, but care is necessary to avoid confusing any original unchanged solid with the desired derivative. A photograph of re-crystallised *p*-toluidine, which has a characteristic appearance, is included.
W. T. CARTER

3316. **Characterisation and principles of determination of laevulic acid.** A. Maurel and J. M. Gastaud (Lab. Municipal de Chim., Nice, France). *Chim. Anal.*, 1959, **41** (12), 469–470.—Qual. reactions for laevulic acid (**I**) are reviewed. The absorption spectrum of the product obtained by treating **I** with *o*-nitrobenzaldehyde in 2 *N* NaOH and extracting with $CHCl_3$ is shown to have a max. at 570 mμ. After descending chromatography on Arches 302 paper for 17 hr. with *n*-butanol - ethanol - water (27:3:10), **I** is detected as a pale-yellow spot with benzidine. Alternatively, the **I** soln. (10%) is treated

with the filtrate from a mixture of equal vol. of 0·5% methanolic hydroxyammonium chloride and 12·5% methanolic NaOH, and boiled for 45 min., then chromatographed. The derivative is revealed as a violet - red spot at $R_F = 0·77$ by spraying with 0·5% ethanolic *p*-dimethylaminobenzaldehyde acidified with conc. HCl and heating for 10 min. at 90° to 95°. The carboxyl group of **I** is titrated with NaOH to phenolphthalein, and the ketone group is determined by titrating with hydroxyammonium chloride to methyl orange and, after boiling, titrating the liberated HCl with 0·5 *N* NaOH. Alternatively, the ketone group can be titrated potentiometrically with hydroxylamine at pH 4·1. E. J. H. Birch

3317. **Separation of aldonic acids by ion-exchange chromatography.** O. Samuelson, K. J. Ljungqvist and C. Parck (Chalmers Tekn. Högsk., Göteborg, Sweden). *Svensk Papp-Tidn.*, 1958, **61** (24), 1043–1049 (in English).—Ion-exchange experiments with xylonic, D-arabonic, D-mannonic, gluconic and D-galactonic acids showed that it is possible to separate and determine each of them. The ion-exchange resin (Dowex 1 or 2) was used in its borate form. The sample soln. were buffered with borate (pH 9) and added to the column, which was washed with 0·005 *M* $Na_2B_4O_7$. The aldonic acids were eluted with $Na_2B_4O_7$ soln. A fraction collector was used and the eluates were analysed by dichromate oxidation. The peaks in the elution curve were identified by paper-chromatographic determination of the sugars formed by borohydride reduction of the eluted acids. The influence of particle size of the resin, concn. of the eluting soln., pH of sample soln., etc., was studied. The recovery of pure aldonic acids amounted to 97·3% to 103·4%. The method was applied to the determination of aldonic acids in a sulphite waste liquor with the following results (in g per litre)—xylonic 1·72, arabonic, 1·35, mannonic 1·44, gluconic 0·31 and galactonic 1·60. B. Rönnholm

3318. **Separation of saturated dicarboxylic acids by chromatography on silica gel.** V. I. Poddubnyĭ. *Izv. Vyssh. Ucheb. Zavedenii. Pishch. Tekhnol.*, 1959, (3), 170–174; *Ref. Zhur., Khim.*, 1960, (3), Abstr. No. 8996.—The column length is 40 cm and the diam. 1 cm. Benzene is used as the mobile phase and ethanol - methanol - H_2O (3:4:3) as the stationary phase. The C_7 to C_9 acids are separated with 0·5 *N* H_2SO_4 as the mobile phase and $CHCl_3$ - *n*-butanol (49:1) as the stationary phase; the elution rate is 0·4 to 0·5 ml per min. The C_3 to C_7 acids are separated with a decreased amount of adsorbent and $CHCl_3$ - butanol (9:1) as the mobile phase. The error is ± 3%. The method is used for the determination of the position of double bonds in fatty acids formed by the hydrogenation of fats and converted into dibasic acids by oxidation. K. R. C.

3319. **High-voltage paper electrophoresis of aliphatic amines and related compounds.** D. Gross (Tate and Lyle Ltd., Keston, Kent, England). *Nature*, 1959, **184** (Suppl. No. 21), 1633–1634.—Sharp separations of closely neighbouring members of a homologous series of amines or diamines or piperazines are rapidly achieved at applied potential gradients of 100 V per cm in suitable equipment (*cf.* Bell *et al.*, *Biochem. J.*, 1959, **71**, 355), in which the temperature and pressure are rigorously controlled and in which diffusion and fluid flow effects are prevented. A. R. Rogers

3320. **Micro-method for differentiation of primary and secondary from tertiary amines by cyanoethylation.** G. W. Stevenson and S. H. Biers (Univ. Calif., Los Angeles, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2095–2097.—When vinyl cyanide is added to an aq. soln. of primary or secondary amine (10^{-2} to 10^{-4} *M*) and heated at 100°, the pH decreases by 0·6 unit or more owing to the formation of the weaker cyanoethylamine bases. Tertiary and some sterically hindered secondary amines do not react. G. P. Cook

3321. **Identification of organic substances. XXXI. Identification of sulphides.** J. Petránek, M. Večeřa and M. Jureček (Res. Inst. Organ. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3637–3642 (in German).—The sulphides are converted into SS-dialkyl-*p*-nitrobenzenesulphonylsulphilimines by reaction with the Na salt of *p*-nitrobenzenesulphonchloramide (Chloramine N) (prep. described) (*cf.* Petránek and Večeřa, *Anal. Abstr.*, 1959, **6**, 1795). The derivatives are separated by column chromatography on silica gel, with formamide as the stationary phase and benzene - *cyclo*hexane (3:2) as the mobile phase. The extraction (10-ml fractions) can be followed by paper chromatography (*loc. cit.*) and the solvent can be distilled off and the recovered derivatives recrystallised and identified by their m.p. The m.p. of 34 derivatives are tabulated. The procedure is illustrated by the separation of a mixture (1:1) of the dibutyl and dipropyl derivatives. J. Zýka

3322. **Gas - liquid chromatographic analysis of mixtures containing methyldiboranes.** G. R. Seely, J. P. Oliver and D. M. Ritter (Dept. of Chem., Univ. of Washington, Seattle, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1993–1995.—Mixtures of methyldiboranes can be almost completely resolved and determined on chromatographic columns of mineral oil on crushed firebrick, operating at 0°. A quant. determination can be carried out by area measurement and is accurate to between 1 and 2% of the components present in a mixture. K. A. Proctor

3323. **Polarographic determination of hexaethyldilead in tetraethyl-lead.** J. E. De Vries, A. Lauw-Zecha and A. Pellecer (Stanford Res. Inst., Menlo Park, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1995–1997.—Hexaethyldilead (**I**) exhibits an anodic wave at $E_{\frac{1}{2}} = -0·24$ V *vs.* the S.C.E., in the solvent system benzene - methanol (1:1, by vol.), with LiCl as the supporting electrolyte. As little as 2 mg of **I** can be determined in 25 ml of tetraethyl-lead. Triethyl-lead chloride can also be determined by means of its cathodic wave, which is exhibited at 0·98 V *vs.* the S.C.E. G. P. Cook

3324. **Determination of isomeric C_9 alkylbenzenes.** S. H. Hastings and D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (12), 2108.—Infra-red quantitative analysis data are given.

3325. **Determination of C_{10} alkylbenzenes.** D. E. Nicholson and S. H. Hastings (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (12), 2107.—Infra-red quantitative analysis data are given.

3326. **Determination of C_{10} to C_{12} alkylbenzenes.** D. E. Nicholson and S. H. Hastings (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (12), 2109.—Infra-red quantitative analysis data are given.

3327. Determination of 1:3- and 1:4-dimethylbenzenes containing benzophenone. S. H. Hastings and D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (12), 2107.—Infra-red quantitative analysis data are given.

3328. Determination of 1:3- and 1:4-dimethylbenzenes in benzonitrile. D. E. Nicholson and S. H. Hastings (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (12), 2108.—Infra-red quantitative analysis data are given.

3329. Separation of the *meta*- and *para*-isomers of the xylenes, cresols and toluidines by gas - solid chromatography. M. A. Hughes, D. White and A. L. Roberts (Gas Res. Dept., Houldsworth School of Appl. Sci., Univ., Leeds). *Nature*, 1959, **184** (Suppl. No. 23), 1796–1797.—A montmorillonite clay in which the Na^+ have been replaced by dimethyldioctadecylammonium ions is used as the stationary phase (*cf.* White, *Anal. Abstr.*, 1958, **5**, 348). A. R. ROGERS

3330. Paper electrophoresis and paper chromatography of phenolic compounds. J. B. Pridham (Chem. Dept., Royal Holloway Coll., Englefield Green, Surrey, England). *J. Chromatography*, 1959, **2** (6), 605–611 (in English).—Paper partition chromatography with plain and molybdate-treated paper and *n*-butanol - ethanol - H_2O (4:1:5) and ethyl acetate - acetic acid - H_2O (9:2:2) solvent systems is described. Aq. sodium molybdate soln. gave a specific spot reaction with phenolic compounds containing the *o*-dihydroxy grouping. Otherwise a diazotised *p*-nitroaniline - NaOH reagent was used to spray the paper. The relative electrophoretic mobilities of 33 phenolic compounds in 5 buffer soln. of pH ranging from 5·2 to 10·0 are tabulated. G. S. ROBERTS

3331. Spot tests for phenol vapours and for aromatic compounds containing oxygen. F. Feigl and E. Jungreis (Min. da Agric., Rio de Janeiro, Brazil). *Anal. Chem.*, 1959, **31** (12), 2099–2101.—The Gibbs indophenol reaction for the detection of phenols by means of 2:6-dichloro-*p*-benzoquinone-4-chlorimine can be applied to phenol vapours. A filter-paper impregnated with the reagent is exposed to the vapour and then to ammonia fumes. With the aid of this procedure it was shown that phenols are split off during the pyrolysis of compounds of phenolic nature, and of aromatic compounds containing O in open or cyclic side-chains. G. P. COOK

3332. Spot tests for phenyl esters and phenyl ethers. F. Feigl and E. Jungreis (Min. da Agric., Rio de Janeiro, Brazil). *Anal. Chem.*, 1959, **31** (12), 2101–2102.—Tests for phenyl esters and phenyl alkyl ethers are based on the fact that they yield phenols when subjected at 150° to pyrolytic saponification and dealkylation, respectively. The resulting phenol vapour is then detected by the Gibbs indophenol colour reaction (*cf. Anal. Abstr.*, 1960, **7**, 3331). G. P. COOK

3333. Determination of isomeric dimethylbenzyl alcohols. D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (12), 2107.—Infra-red quantitative analysis data are given.

3334. Determination of cyclic ketones by paper chromatography. V. Dudek and J. Stuchlík (Dept. of Org. Chem., Inst. Chem. Technol., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3797–3799 (in Russian).—A mixture of *cyclo*pentanone and its homologues with 6, 7, 8, 9, 10 and 12 C atoms was separated chromatographically after conversion into the corresponding 2:4-dinitrophenylhydrazones. The separation was carried out on Whatman No. 1 paper impregnated with kerosine (boiling-range 200° to 220°) - light petroleum (boiling-range 30° to 45°) (2:3). The following solvent systems were used—for the descending technique, methanol - H_2O - acetic acid (85:15:2), (90:10:3) and (95:5:3); for the ascending technique, 80% methanol, and methanol - H_2O - acetic acid (40:10:1). About 6 μg of 2:4-dinitrophenylhydrazones dissolved in $CHCl_3$ were thus separated. The intensity of the yellow spots can be increased by moistening them with KOH soln. or by observation in u.v. light. J. ZÝKA

3335. Mass-spectrometric analysis. Aromatic acids and esters. F. W. McLafferty and R. S. Gohlke (Spectroscopy Lab., The Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2076–2082.—Data are given on 50 aromatic acids and esters and can be used for the identification, analysis and structural determination of such compounds. A summary of some common major ions is useful for mol. structure determination. K. A. PROCTOR

3336. Separation of isomeric phthalic acids by partition paper chromatography. L. V. Golosova (State Sci. Res. and Design Inst. of the Nitrogen Ind. and Synthetic Org. Products, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (6), 748.—A mixture of tere- and *iso*-phthalic acids is separated by ascending paper chromatography for 10 to 15 hr. with propanol - 3·5% aq. NH_3 - water (350:12:105). The chromatogram is dried at 40° to 50° or at room temp. and sprayed with an aq. soln. of bromothymol blue adjusted to pH 8 with alkali; sharply defined yellow spots appear on a blue background. These are marked with pencil since, on further drying, even *in vacuo*, the blue colour changes to pale yellow. The dried chromatogram is attached to a fluorescent screen and irradiated with u.v. light; shadows due to absorption of the radiation indicate the positions of the spots. The R_F values for the separated acids are in good agreement with those given by the pure compounds. C. D. KOPKIN

3337. Fluorescence method for the determination of gallic acid. G. A. Kisilevich. *Ukr. Khim. Zhur.*, 1959, **25** (2), 237–238; *Ref. Zhur., Khim.*, 1960, (3), Abstr. No. 9008.—The fluorescence of an alkaline aq. gallic acid soln. is measured in filtered u.v. light. The gallic acid concn. range covered is 0·001 to 0·1%, and the optimum is 0·01 to 0·1%. The best results are obtained by a volumetric method based on the discharge of the fluorescence by aq. $CuSO_4$ soln. (0·3928 g per litre). The test soln. is diluted 1:1, 1:2, 1:5, 1:10, etc.; aq. NH_3 soln. (0·1 to 0·5 ml) is added to each of these dilutions (1 ml) to obtain a pH of 9 to 10 and the dilution giving a bright-green fluorescence is selected for titration with $CuSO_4$ to an end-point indicated by the discharge of the fluorescence; the gallic acid content is calculated from the $CuSO_4$ titre. The sensitivity of the method is 0·01 mg per ml and the error is 3%. K. R. C.

3338. **Determination of anhydrides derived from dimethylbenzoic acids.** D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (12), 2108.—Infra-red quantitative analysis data are given.

3339. **Determination of isomeric methylbenzyl benzoates.** D. E. Nicholson (Humble Oil & Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (12), 2108.—Infra-red quantitative analysis data are given.

3340. **Colour reaction for determination of some *m*-dinitro aromatic compounds.** J. P. Heotis and J. W. Cavett (Dr. Salsbury's Lab., Charles City, Iowa, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1977–1978.—The colour reactions of various *m*-dinitro compounds in dimethyl sulphoxide solvent with diethylamine reagent were investigated. The magnitude of the extinction of some of the compounds was sufficient to serve as a means of assay, and the free acids of the compounds did not give a colour with the reagents used. All of the 3:5-disubstituted compounds which reacted gave maximum absorption in the 540 to 575-mμ region, and most of the 2:4-disubstituted compounds absorbed at 640 to 695 mμ. G. P. Cook

3341. **Quantitative determination of ethyl-2:4-dinitrobenzene in ethylnitrobenzene.** O. S. Vladýrchik, L. L. Bespalova and P. M. Kochergin. USSR Pat. No. 119,524; 10th May, 1959.—Ethylnitrobenzene (**I**) gives a pale greenish-yellow colour with an aq. acetone soln. of NaOH; in the presence of ethyl-2:4-dinitrobenzene (**II**) a blue colour is formed, the intensity being proportional to the concn. of **II**. *Procedure*—To 0·2 ml of water-washed technical neutral **I** add 5 ml of acetone and 10 drops of 2 *N* NaOH and shake. A greenish-yellow colour is formed which, in the presence of **II**, becomes blue within 5 min., the colour being violet at higher concn. of **II**. Compare the colour formed with that of standard samples of **I** containing from 0·05 to 2·0% (w/w) of pure **II**. C. D. Kopkin

3342. **Ultra-violet and infra-red spectra of some aromatic nitro compounds.** C. P. Conduit (Min. of Supply, E.R.D.E., Waltham Abbey, Essex, England). *J. Chem. Soc.*, 1959, 3273–3277.—Ultra-violet spectra (in the range 210 to 280 mμ) and i.r. spectra (in the range 1300 to 1600 cm^{-1}) are investigated for all isomers of mono-, di- and tri-nitrobenzenes and -toluenes (except 1:2:3-trinitrobenzene). Introduction of a second nitro group decreases the conjugation by increasing competition for electrons of the ring and results in a hypsochromic shift in the u.v. This shift is increased with *ortho*-pairs of nitro groups probably owing to simultaneous twisting out of the plane of the ring nearly destroying the conjugation. *m*- and *p*-Nitrotoluenes show a bathochromic shift due to increased availability of electrons from the ring, but in *o*-nitrotoluene this is compensated by the steric effect. An attempt is made to correlate the shifts in dinitrotoluenes as additive functions of the shifts in mononitrotoluenes and dinitrobenzene. This is fairly successful, but becomes impossible with trinitrotoluenes. The i.r. spectra show a splitting of the symmetrical band (of the NO_2 group) wherever one nitro group is strongly hindered. The asymmetric band frequencies fall into three ranges: mononitro- 1509 to 1540 cm^{-1}, dinitro- 1539 to 1552 cm^{-1}, and trinitro- 1554 to 1567 cm^{-1}, though strong electron donor groups such as NR_2 may interfere with this classification. The integrated band intensities are less obviously correlated with the position of groups. The symmetric band width of an isolated nitro group is 8 to 11 cm^{-1}, but the presence of small hindering groups (CH_3 or C_2H_5) broadens the band towards 19 cm^{-1} without change of frequency, but large blocking groups lead to broadening and rise in frequency of the band. E. J. H. Birch

3343. **Solvent effects in the spectrophotometric determination of weak organic acids in alkaline solution. Application to aromatic primary amine and carbonyl derivatives.** E. Sawicki, T. R. Hauser and T. W. Stanley (Air Pollution Engng Res., Robert A. Taft Engng Center, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2063–2065.—The effect of the solvent on the wavelength of the absorption max. and on the colour intensity has been studied. The application of these effects to the analysis of aromatic primary amines and ketones is described. K. A. Proctor

3344. **Pinakryptol Yellow—a specific reagent for the detection of arylsulphonic acids on chromatograms.** J. Borecký (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *J. Chromatography*, 1959, **2** (6), 612–614 (in German).—A sensitive method for the identification of arylsulphonic acids is described. Paper chromatograms, prepared by the descending technique, with *n*-propanol - aq. NH_3 (2:1) as solvent, are sprayed with an aq. 0·05% soln. of Pinakryptol Yellow (Höchst) and then examined in u.v. light. Characteristic yellow or orange fluorescent spots on a pale-green background are obtained. G. S. Roberts

3345. **Study of the sulphonation reaction. I. Determination of toluenedisulphonic acid isomers.** A. A. Sprýskov and T. I. Potanova. *Izv. Výssh. Ucheb. Zavedenií. Khim. i Khim. Tekhnol.*, 1959, **2** (1), 41–45; *Ref. Zhur., Khim.*, 1959, (22), Abstr. No. 78,388.—A quantitative analysis of mixtures of toluene-2:4- (**I**), -2:5- (**II**), -2:6- (**III**), -3:5-disulphonic acid (**IV**) and H_2SO_4, based on the pptn. of salts of **II** and **III** with 2-naphthylamine (**V**), and of **II** with benzidine (**VI**), and on the determination of the melting-point of the mixture of the sulphonyl chlorides of **I** and **IV** has been developed. Semi-quantitative solubility data of the salts of **I**, **II**, **III** and **IV** in 18 arylamines have been obtained and a thermal diagram for the binary system of toluene-2:4- and -3:5-disulphonyl chloride has been prepared. *Procedure*—Dissolve $\simeq$ 5 g of the test sample in water and make up to exactly 250 ml with water; take a 10-ml aliquot and titrate with 0·1 *N* NaOH, with methyl red as indicator (this gives total acidity). Dilute the neutral soln. to 250 ml, precipitate SO_4^{2-} as $BaSO_4$ in the presence of NH_4Cl and calculate H_2SO_4 and the toluene-disulphonic acid content in the test sample. To determine **II** plus **III** (*a*%), heat a 100-ml aliquot of the test soln. to boiling and neutralise with $BaCO_3$ to methyl red, filter off the $BaSO_4$ ppt., wash it with hot water, and evaporate the combined washings and filtrate to 120 ml. Add to this soln. 120 ml of a saturated soln. of **V** hydrochloride, maintain for 3 hr. at 0°, then filter off the ppt., wash it with ice-cold water and titrate the filtrate with 0·1 *N* NaOH to phenolphthalein. Then $a = 0{\cdot}03152b$, where b = ml of NaOH soln. Make the soln. obtained alkaline, leave it for 2 hr. at 0°, filter off **V**, evaporate the

filtrate to $4b$ ml, add $2b$ ml of **VI** hydrochloride soln., maintaining the temp. at $\simeq 50°$ during the addition, filter off the ppt. of the benzidine salt of **II** after $\simeq 2$ hr., wash the ppt. with ice-cold water and titrate the filtrate with 0·1 *N* NaOH to phenolphthalein. Calculate the content (c %) of **II** in the test sample from the formula $c = 0{\cdot}03152d$, where d = ml of NaOH soln.; calculate the amount of **III** by difference. Neutralise the filtrate (after pptg. salts of **II** and **III** with **V**) with NaOH soln. to phenolphthalein, let it stand for 1 hr. at 0°, filter off **V**, remove remaining **V** by heating with charcoal. Evaporate the filtrate to dryness, dry the residue at 180°, heat it with PCl_5 for 1 hr. to convert the toluenedisulphonic acids into sulphonyl chlorides and determine the ratio of **I** and **II** by reference to the thermal diagram. Apply the following empirical correction factors to the results obtained: + 0·5% for **II** and **IV**, + 0·7% for **III** and − 1·5% for **I**. The maximum error is $\pm$ 1·5% of the sum of the toluenedisulphonic acids. Monosulphonic acid interferes with the determination of **III**, and trisulphonic acids with the determination of **I** and **IV**. W. Roubo

3346. **Photometric determination of 1-naphthylamine-4-sulphonic acid in technical 1-naphthol-4-sulphonic acid.** E. S. Levin and E. I. Burtseva (K. E. Voroshilov Sci. Res. Inst. of Org. Intermediates and Dyestuffs, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (6), 732–734.—The method is based on the simultaneous nitrosation of 1-naphthol-4-sulphonic acid (**I**) and diazotisation of 1-naphthylamine-4-sulphonic acid (**II**), coupling the diazo compound with 8-amino-1-naphthol-2:4-disulphonic acid (**III**) and photometric determination of the resulting dyestuff. First determine total **I** and **II** with nitrate ($\equiv q$ %); then take ($246{\cdot}2 \times 0{\cdot}005 \times 100/q$) g of sample, dissolve it in 500 ml of water and filter if necessary. To 50 ml of this soln. add 50 ml of water, heat to 40° to 45° and add almost all the required amount of 0·2 *N* $NaNO_2$; then add, with stirring, 2 ml of conc. HCl, and titrate with 0·2 *N* $NaNO_2$ to a colour with starch - iodide that is stable for 10 min. To a 500-ml flask add 5 ml of 0·02 *M* **III**, 100 ml of water and 3 g of $NaHCO_3$. When dissolution is complete add the diazo compound slowly, with stirring, set aside for 20 min., make up to vol. and measure the extinction at 580 mμ against a blank, diluting if necessary. Determine the content of **II** from a calibration curve prepared similarly, with 0·002 *M* **II** (sodium salt) and 0·01 *M* **I** (zinc salt). The max. error is $\pm$ 0·25% abs. C. D. Kopkin

3347. **Chromatography of aromatic isomers. XII. Paper-chromatographic separation of chloronitronaphthalenes.** J. Franc (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, **24** (11), 3624–3628 (in German).—The $\triangle R_F$ changes (caused by resonance-energy changes) and the $\triangle K_{Cl}$- value of various isomers of chloronitronaphthalene were studied. The separation was carried out by the descending technique on Whatman No. 1 paper impregnated with petroleum (boiling-range 190° to 275°), diethylformamide, dimethylformamide or acetamide, with 80% aq. ethanol or *cyclo*hexane as mobile phase. The R_F values of 11 chloronitronaphthalene derivatives are tabulated. The samples (10 to 25 μg) were dissolved in $CHCl_3$, and the separated spots were detected in u.v. light (discharge of the fluorescence) or with *p*-dimethylaminobenzaldehyde after reduction with $SnCl_2$ soln. J. Zýka

3348. **Colour reaction for detecting and determining chromones and related compounds.** J. S. King, jun., and N. H. Leake (Res. Dept., The S. E. Massengill Co., Bristol, Tenn., U.S.A.). *Analyst*, 1959, **84**, 694–699.—For the determination, aliquots of a soln. of the weighed sample in $CHCl_3$ are evaporated to dryness by means of a current of air. To each residue are added an ethanolic soln. of *m*-dinitrobenzene and ethanolic KOH soln. After 5 min., aq. ethanol is added and the colour is measured against a reagent blank. The colours produced by a large number of chromones and related compounds are tabulated. For chromones to produce the characteristic blue to purple - blue colour there must be a methyl or methylene group in the 2-position, and not more than one hydroxyl group in the benzene ring and that not in the 2- or 3-position. Methoxyl, methyl and halogen substituents do not interfere. With slight differences in detail the reaction is used for the qualitative detection of the compounds. A. O. Jones

3349. **Colorimetric determination of carbazole.** G. Gilbert, R. M. Stickel and H. H. Morgan, jun. (U.S. Steel Corp., Monroeville, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1981–1983.—The method is based on the reaction of carbazole with xanthhydrol and glacial acetic acid in the presence of HCl; the extinction of the product is measured at 525 mμ. The coeff. of variation is $\pm$ 0·6% and good agreement was reached with the results obtained by i.r. analysis. The substances common to carbazole fractions of coal tar show almost no interference. Evidence is presented which suggests that the coloured product is an xanthylium salt, and the mechanism for its formation is postulated. G. P. Cook

3350. **Paper chromatography of indole derivatives.** Ž. Procházka, V. Šanda and K. Macek (Dept. Natural Products, Chem. Inst., Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (9), 2928–2937 (in German).—The R_F values of 74 indole derivatives in various solvents were determined. The "group constants" for some of the solvent systems used were calculated and the relation between the R_F values and the structures of the compounds is discussed. Whatman No. 4 paper was used for the aq. systems and Whatman No. 2 paper (impregnated with a 50% ethanolic soln. of formamide) for the formamide systems. The following solvent systems were studied—light petroleum - methanol - H_2O; CCl_4 - acetic acid - H_2O; di*iso*propyl ether - H_2O; butyl acetate - H_2O; $CHCl_3$ satd. with formamide; benzene satd. with formamide; *cyclo*hexane satd. with formamide; *iso*propyl alcohol - aq. NH_3 - H_2O. For detection, formaldehyde soln. - HCl (1:1), 2:4-dinitrophenylhydrazine, and Ehrlich's, Salkowski's and Jaffé's reagents were used. J. Zýka

3351. **Application of nitrometry. XVIII. Determination of pyridine and its derivatives.** Makoto Yokoo (Res. Lab., Takeda Pharm. Industries Ltd., Osaka). *Chem. & Pharm. Bull., Japan*, 1959, **7** (8), 884–886 (in English).—To the sample of pyridine, *iso*nicotinic acid, 2-benzylaminopyridine or *iso*-nicotinamidoethanol (0·25 to 0·5 millimole) in aq. soln. (2 ml) add a suspension of activated Raney nickel (2 g) in water (2 to 3 ml) and heat at 80° to 90° for 2 hr., with shaking. Allow to cool, filter, and wash the ppt. with water. Dilute the combined filtrate and washings to 20 ml and determine secondary amines in a 2-ml aliquot by the

method described previously (*cf. Anal. Abstr.*, 1958, **5**, 3785). The accuracy is within ≃ 1·3%.
A. R. ROGERS

3352. **Determination of pyridine and its derivatives with cyanogen chloride and barbituric acid.** W. Nielsch and L. Giefer (Anal. Lab., Joh. A. Benckiser G.m.b.H., Ludwigshafen/Rhein, Germany). *Z. anal. Chem.*, 1959, **171** (6), 401–409 (in German).—Pyridine (**I**), γ-picoline (**II**) and *iso*nicotinic acid (**III**) condense with cyanogen chloride and barbituric acid at pH 5·0, and the colours so formed may be used to detect and determine these compounds. To a 25-ml flask are added successively 1·25 ml of acetate buffer soln. (pH 5·0), 0·5 ml of KCN soln. (10% aq.), 2·5 ml of chloramine T soln. (10% aq.), sufficient acetic acid to bring the pH to 5·0, 6·25 ml of barbituric acid soln. (2% aq. adjusted to pH 5·0), 2·5 ml of acetone and the test soln. The mixture is made up to vol., and the extinction is measured after 1 hr. at 578 mμ for **I** and 598 mμ for **II** or **III**. Mixtures of **I** and **II** or **I** and **III** can be determined in microgram amounts. By reducing all volumes to one-tenth, as little as 0·01 μg of **I** can be determined. Pyridine derivatives separated on paper chromatograms can be detected by spraying with aq. barbituric acid and exposing to cyanogen chloride vapour. H. M.

3353. **Analysis of light hydrocarbons.** G. R. Primavesi (Distillers Co. Ltd., Great Burgh, Surrey, England). *Nature*, 1959, **184** (Suppl. No. 26), 2010–2011.—One 4-ft. column was packed with tri-*iso*butylene on Celite (85 to 100 mesh) and a similar column was packed with ethanediol containing 27% w/w of $AgNO_3$. These columns were used (*a*) separately, (*b*) in series (tri*iso*butylene second), and (*c*) with a mixture of the two packings to obtain values for the specific retention volumes of ethane, ethylene, propane and propylene. The temperature used was 12°, the inlet pressure was 50 torr for single 4-ft. columns and 100 torr for combined 8-ft. columns, and the outlet pressure atmospheric. Nitrogen at a flow rate of 20 ml per min. was used as carrier gas. Barnard and Hughes (*Ibid.*, 1959, **183**, 250) claimed that a gas-chromatographic separation of these hydrocarbons was successful on a mixed column, but not in two separate columns in series. The present study on separate columns indicated that most of the tri*iso*butylene was in fact lost during the mixing operation, because of its appreciable volatility at the temperature used. It is therefore suggested that Barnard and Hughes obtained their separation not on a "mixed" column, but on a column containing ≃ 90% of ethanediol - $AgNO_3$ and 10% of tri*iso*butylene. S. BAAR

3354. **Chromatographic analysis of C_5 hydrocarbon mixtures.** A. A. Zhukhovitskiĭ, B. A. Kazanskiĭ, A. I. Karÿmova, P. S. Pavlova, O. D. Sterligov and N. M. Turkel'taub (All-Union Sci. Res. Geological Prospecting Petroleum Inst., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (6), 721–728.—Mixtures of C_5 hydrocarbons are analysed with air as carrier gas by a combination of "chromathermography" on alumina and gas - liquid partition chromatography on diatomaceous earth containing 25% of dibutyl phthalate. The exit gases were detected by thermal conductivity, the order and time of appearance of the individual components being determined from the individual substances and from synthetic mixtures. Of all the possible mixtures of C_5 hydrocarbons, only that of 3-methylbut-1-ene with *iso*pentane is not separated by the combined method, but either method alone separates the mixture. The method has been used to analyse the dehydrogenation products of *iso*pentane and light petroleum fractions. By using 10 to 15 ml of sample, the method can measure tenths of a per cent. of a component; by using 100 to 200 ml, this percentage can be substantially reduced. C. D. KOPKIN

3355. **Analysis of mixtures of C_5 to C_7 hydrocarbons by gas - liquid chromatography.** D. A. Kondrat'ev, M. A. Markov and Kh. M. Minachev (N. D. Zelinskiĭ Inst. of Org. Chem., Acad. Sci. USSR). *Zavod. Lab.*, 1959, **25** (11), 1301–1304.—Complete separation of C_5 to C_7 mixtures of paraffins, naphthenes and aromatic hydrocarbons by means of two successive three-metre columns, one containing tritolyl phosphate and brick and the other dioctyl phthalate and brick, is reported. For the first 50 min. the temp. is kept at 15° to 20° which permits the separation and detection of all C_5 to C_6 normal and isoparaffins. The temp. is then raised to 85° at the rate of 1·5° per min. The total time taken is from 2 to 2·5 hr. Hydrogen is passed at the rate of 60 ml per min. Detection is by means of a specially designed flame detector.
G. S. SMITH

3356. **Composition of crude oil through seven carbons as determined by gas chromatography.** R. L. Martin and J. C. Winters [Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1959, **31** (12), 1954–1959.—A gas-chromatographic pre-fractionator column (containing 18% of Apiezon L on firebrick) separates the components containing from two to seven C atoms from the crude oil and transfers them to one of three analyser columns where the desired individual separations are made. A separate sample is pre-fractionated into each of the three copper analyser columns (0·25 in. in diam.): a 26-ft. copper column containing 13·4% of *iso*quinoline and a 40-ft. column containing 3·1% of 1-chloronaphthalene are used to determine the saturated hydrocarbons and benzene, and a 12-ft. column containing 5% of ββ′-oxydipropionitrile for determining toluene. The coeff. of variation for 14 components on a synthetic sample averaged ± 1·8% (six determinations) of the amount present. The need for accurately measuring the sample is eliminated by adding a known quantity of a reference compound. Twenty crude oils were analysed and the data are listed. G. P. COOK

3357. **Development of molar volume equation for structural analysis of hydrocarbons.** M. L. Boyd and D. S. Montgomery (Fuels Div., Mines Branch, Dept. of Mines and Tech. Surveys, Ottawa, Canada). *J. Inst. Petrol.*, 1959, **45**, 345–358.—The C atoms in a hydrocarbon mol. are grouped under five structural types each adding its characteristic increments (v) to the molar volume (V at 20°/1 atm.). Thus the mol. may contain c_1 paraffinic C atoms in linear or branched chains, c_2 alicyclic C atoms which are not, and c_3 which are, junctions of fused saturated rings, and c_4 aromatic C atoms which are not, and c_5 which are, junctions of fused aromatic rings. If all the C atoms are of one class, $V = v_x c_x + k_x$, where k/c represents the effect of mol. wt. on the contribution to V per atom of that class. Data for **13** *n*-paraffins gave $V = 16{\cdot}38c_1 + 30{\cdot}61$, for four naphthenes $V = 13{\cdot}20c_2 + 28{\cdot}48$, and for three aromatics $V = 12{\cdot}406c_4 + 14{\cdot}042$. v_3 and v_5 were

calculated additively from data for hydrocarbons containing mixed types (c_1 + c_4) and (c_2 + c_6). By comparing values of V calculated additively with experimental values, correction terms for the interaction of certain pairs of types were found, and are incorporated in the final equation: $V = c_1(16{\cdot}38 + 30{\cdot}61/\Sigma c) + c_2(13{\cdot}20 + 28{\cdot}48/\Sigma c) + c_3(10{\cdot}981 + 20{\cdot}679/\Sigma c) + c_4(12{\cdot}406 + 14{\cdot}402/\Sigma c - 1{\cdot}96\,c_1/\Sigma c + 10{\cdot}13\,c_3/\Sigma c) + c_5(5{\cdot}124 - 5{\cdot}238/\Sigma c)$. The equation gives values for 130 known hydrocarbons with mean error ± 0·66%; the deviations indicate that the junction points of non-fused naphthenic (c_6) or aromatic (c_7) rings should be treated as distinct types, and require the addition to the calculated value of V of correction terms $c_6(13{\cdot}24 + 17{\cdot}69/\Sigma c)$ and $c_7(7{\cdot}04 + 16{\cdot}53/\Sigma c)$. Further interaction terms remain to be calculated as data become available. A. R. PEARSON

3358. **Development of molar refraction equation for structural analysis of hydrocarbons.** M. L. Boyd and D. S. Montgomery (Fuels Div., Mines Branch, Dept. of Mines and Tech. Surveys, Ottawa, Canada). *J. Inst. Petrol.*, 1959, **45**, 359–372.—An equation analogous in form to that for the molar volume (*cf. Anal. Abstr.*, 1960, **7**, 3357) gives the molar refraction (R for D/20°) in terms of the increments contributed by C atoms belonging to five different structural types. The final equation, with correction terms for interactive effects, is: $R = c_1(4{\cdot}623 + 2{\cdot}314/\Sigma c) + c_2(4{\cdot}468 + 0{\cdot}868/\Sigma c - 0{\cdot}245c_1/\Sigma c) + c_3(3{\cdot}693 + 0{\cdot}3395/\Sigma c) + c_4(4{\cdot}5445 - 1{\cdot}021/\Sigma c - 0{\cdot}396c_1/\Sigma c - 5{\cdot}701c_3/\Sigma c) + c_5(5{\cdot}734 - 14{\cdot}333/\Sigma c)$. As for the molar volumes, C atoms forming junction points of unfused rings require additional terms, $c_6(4{\cdot}105 - 3{\cdot}634/\Sigma c)$ for naphthenes and $c_7(2{\cdot}872 + 5{\cdot}405/\Sigma c)$ for aromatics. For the use of the molar volume and refraction equations in structural analysis, see Montgomery and Boyd, *Anal. Chem.*, 1959, **31**, 1290. A. R. PEARSON

3359. **Determination of arsenic in petroleum stocks and catalysts by evolution as arsine.** D. Liederman, J. E. Bowen and O. I. Milner (Socony Mobil Oil Co., Inc., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2052–2055.—For liquid stocks, the As is extracted and simultaneously oxidised by a mixture of H_2SO_4 and H_2O_2, and then, after addition of zinc metal, evolved as AsH_3, which is absorbed in a soln. of Ag diethyldithiocarbamate in pyridine. The extinction of this soln. is measured at 540 mμ. For catalyst samples the material is first made soluble by fusion with Na_2O_2. Recoveries of added As in the range 2 to 79 parts per thousand million ranged normally from 80 to 120%, and as little as 0·03 μg could be detected. G. P. COOK

3360. **Determination of sulphur and chlorine in petroleum liquids by X-ray fluorescence.** T. C. Yao and F. W. Porsche [Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1959, **31** (12), 2010–2012.—A commercial X-ray spectrograph equipped with a rock-salt crystal, helium path, flow proportional counter and pulse height analyser, was used to determine the chlorine and sulphur content of petroleum, residual and distillate fuels, lubricating oil additives, insecticides and herbicides. The limit of detection is 0·002% by wt. and the precision compares well with that of the ASTM bomb and high-temperature combustion methods. G. P. COOK

3361. **Determination of dissolved gases in petroleum fractions by gas chromatography.** J. A. Petrocelli and D. H. Lichtenfels (Gulf Res. & Development Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2017–2019.—The method described has been used for the determination of oxygen, nitrogen and other dissolved gases in a variety of samples, including pure hydrocarbons in the C_5 to C_{10} range, catalytic feedstocks, and lubricating oils of various viscosities. An essential feature of the method is the use of a pre-column of silica gel or crushed firebrick to retain hydrocarbons. The oxygen and nitrogen are resolved on a 10-ft. column of Linde 5A Molecular Sieve pellets of 20 to 30-mesh size. Helium is used as the carrier gas, and detection is carried out by a thermal conductivity cell. Results obtained by this procedure compare well with those by other methods. K. A. PROCTOR

3362. **Determination of trace hydrocarbon impurities in petroleum benzene and toluene by gas chromatography.** F. A. Fabrizio, R. W. King, C. C. Cerato and J. W. Loveland (Sun Oil Co., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2060–2063.—Hydrocarbon impurities in toluene are determined on a 25-ft. column of 20% w/w of 2:4:7-trinitrofluorenone on 30 to 60-mesh C22 firebrick at 160°, with He as the carrier gas. Impurities in benzene are determined on a 10-ft. column, packed with two separate stationary phases. The inlet half of the column contains 40% w/w of a saturated soln. of picric acid in di-*n*-butyl phthalate on 30 to 60-mesh C22 firebrick, whilst the exhaust half contains 15% w/w of di-*n*-decyl phthalate on C22 firebrick to retain any picric acid distilling from the inlet half. This column operates at 120°, with He as the carrier gas. The limit of detection is about 0·01% v/v of an impurity, and in the range 0·06 to 0·4% v/v the accuracy is 0·01%. K. A. PROCTOR

3363. **Rapid methods for the analysis of petroleum cokes.** A. L. Conrad and J. K. Evans [Standard Oil Co. (Ohio), Cleveland, U.S.A.]. *Anal. Chem.*, 1959, **31** (12), 2015–2017.—Careful control of the burning conditions by means of an induction furnace enables the volatile matter and ash content to be determined in about 1 hr., and subsequent colour development of several metals can be carried out on a soln. of the fused ash. The results deviated from those obtained by the ASTM method by 0·4 and 0·01% for the volatile matter and ash content, respectively. G. P. COOK

3364. **Gas-liquid chromatographic analysis of aromatic hydrocarbons boiling up to 218° in a low-temperature coal-tar.** Ta-Chuang Lo Chang and C. Karr, jun. (Bur. of Mines, U.S. Dept. of Interior, Morgantown, W. Va., U.S.A.). *Anal. Chim. Acta*, 1959, **21** (5), 474–490.—Fifty-two aromatic hydrocarbons (including indanes, benzofurans, indenes and methylated, ethylated and propylated benzenes) were separated and identified by gas chromatography at 150° on a coiled column (15 ft. by 0·25 in.) of 25% Apiezon-L grease on firebrick (30 to 60 mesh). The carrier gas was He at a pressure of 12 lb per sq. in., and the fractions were collected in 6-in. syringe needles kept at 0° and connected to the syringe-adaptor of the Perkin-Elmer Vapour Fractometer. The i.r. spectrum of the fraction was then obtained in a 0·05- or 0·1-mm cell to identify the components. Identification was confirmed from the correlation between retention times and b.p.

By using *n*-propylbenzene as internal standard, quant. determinations were made of 43 compounds having b.p. $< 200°$; the percentages by wt. varied from 0·001 to 0·26. Those alkylbenzenes having an equal number of C atoms in their alkyl groups show a linear relation between log relative retention and b.p.; the C_3 to C_{12} alkylbenzenes lie on five parallel lines separated by a distance that is a function of the logarithm of the number of C atoms (2 to 6) in the alkyl group. This correlation, which is useful for identifying peaks in the chromatogram, does not hold for indenes, styrenes and naphthalene.

W. J. BAKER

3365. **Determination of trace elements in lignite ashes.** R. L. O'Neil and N. H. Suhr (Coll. Mineral Ind., State Univ., University Park, Pa.). *Appl. Spectroscopy*, 1960, **14** (2), 45–50.—The Stallwood jet source (*J. Opt. Soc. Amer.*, 1954, **44**, 171) is adapted to the analysis of the non-volatile components of lignite ashes, with the substitution of CO_2 gas for the air jet. Advantages claimed are suppression of CN bands, thus increasing the usable spectrum band, improvement of the line-to-background ratio, and provision of a more precise technique for determination of the non-volatile elements. Standards are prepared by doping a representative base mixture containing SiO_2 50%, Fe_2O_3 15·0%, Al_2O_3 12·0%, MgO 1·5%, CaO 12·0%, K_2O 1·3%, Na_2O 8% and U_3O_8 0·2% to cover an impurity range of 0·0005 to 1·0%. An internal standard of 2·5% of Lu_2O_3 is added to a buffer mixture of $CaCO_3$ and fused K_2SO_4 (1:1). The arcing mixture contains 1 part of buffer to 10 parts of lignite ground in an agate mortar for 10 min. to which is added 20 parts of pure graphite powder, the whole being ground for 5 min. A 32 ± 1 mg charge is packed into a U.C. Products, type 5790 carbon electrode, with a ¼-in. pointed carbon counter-electrode, and burned to completion. Precision studies for eighteen elements indicate a coeff. of variation of $\pm$ 2 to 12%. The volatile elements As, Pb, Sn, Ag, Zn and Ga are determined by a d.c. arc technique on pressed-pellet samples. A 40-mg pellet mixture, composed of 1 part of internal standard, 10 parts of sample and 1 part of S.P.-1 graphite is arced for 50 sec. at 12 amp. The internal standard is 0·5% of Sb_2O_3 plus 1·4% of CdO added to fused K_2SO_4. These techniques have been tested on U.S. Geological Survey standard rock samples G1 and W1. Results indicate the accuracy and the applicability of the method to a wide range of silicate analyses.

G. P. MITCHELL

3366. **The determination of tar acids and tar bases in light coal-tar distillates.** G. E. Mapstone and A. T. Keppie (S. African Torbanite Mining and Refining Co., Ltd., P.O. Box 5083, Boksburg North). *Chem. & Ind.*, 1959, (45), 1397–1399.—Sources of error in the STPTC (Standardisation of Tar Products Technical Committee) methods are discussed. The following procedure is proposed. Wash 50 ml of the sample in a 100-ml burette with 0·25 *N* HCl (3 × 25 ml) and once with water. Combine the washings. Observe the shrinkage of the sample. Determine the water content of the original sample. Distil the washings, collecting 50 ml in a graduated separating-funnel. Run off the aq. layer into a flask and wash the oily layer with HCl (2 ml). Read the vol. of oil. Neutralise the combined aq. layer with $Ba(OH)_2$ and 0·1 *N* HCl to phenolphthalein and titrate with 0·1 *N* HCl to screened methyl orange. Read the vol. of phenols in the distillation residue after acidification, taking care to add sufficient NaCl. Wash the sample remaining in the burette with 2 *N* HCl (3 × 25 ml). Observe the shrinkage. Titrate the washings, with the two indicators, as described above.

G. BURGER

3367. **Automatic apparatus for the detection and recording of oxides of nitrogen in coke oven gas.** J. Pierrain. *Chim. Anal.*, 1959, **41** (12), 477–485.—The necessity for the control of oxides of N in coke oven gases, especially when liquefaction is to be carried out, is discussed. Methods of determining oxides of N are discussed and a continuous method is described. *Procedure*—The gas is pumped (15 litres per hr.) through a cell in which oxygen is generated electrolytically, the dimensions being such as to allow the optimum time of contact for the oxidation of NO to N_2O_3 and N_2O_5. The gas then passes to an absorption tube fed with Griess-Ilosvay reagent at a rate controlled by the gas pump motor. The reagent (stored under H also provided by the electrolysis apparatus) flows through the reference cell of a balanced bridge circuit incorporating two photo-resistive cells, then through the absorber and then through the test cell so that the colour produced in the reagent throws the bridge out of balance. In making up the reagent, the naphthylamine hydrochloride must be very pure, the water must be distilled over permanganate or de-ionised and the acetic acid must not be added until immediately before use. The range of sensitivity is 0 to 0·250 mg per cu. metre.

E. J. H. BIRCH

3368. **Determination of total fat by a complexometric method and the excess alkalinity in diluted soap.** I. G. Izhak, S. K. Kel'manzon and N. V. Izotova ("Apatit" Combine). *Zavod. Lab.*, 1959, **25** (11), 1299–1300.—The sample (100 g) is mixed with 40 ml (or more if the content of total fat is $> 3·5\%$) of 0·5 *N* $CaCl_2$ until the calcium soap is coagulated, and then diluted to 500 ml. An aliquot (100 ml) of the filtered soln. is titrated with 0·1 *N* HCl to methyl orange to give the excess alkalinity, and the excess of $CaCl_2$ is then titrated with 0·1 *N* EDTA (disodium salt) after addition of an ammoniacal buffer soln. and Acid Chrome dark blue (C.I. Mordant Black 17) as indicator.

G. S. SMITH

3369. **Determination of ionic surface-active agents with dyes. I. Erythrosin and eosin methods.** Masaru Aoki and Yoji Iwayama (Pharm. Fac., Osaka Univ., Toyonaka, Osaka-fu). *J. Pharm. Soc. Japan*, 1959, **79** (4), 522–526.—Anionic surface-active agents (5 to 20 mg), such as sodium alkyl sulphate and alkylarylsulphonate, are dissolved in citric acid - Na_2HPO_4 buffer (pH 4·5) (20 ml) and titrated with 0·005 *M* cationic surface-active agent soln., prepared from benzalkonium chloride, in the presence of $CHCl_3$ (10 ml) and erythrosin or eosin as indicator. The $CHCl_3$ layer changes sharply to crimson at the end-point and the accuracy of the titration is within $\pm$ 0·2%. By the use of back-titration, this method is applicable to the determination of cationic surface-active agents such as invert soaps and long-chain aliphatic amine salts. McIlvain's buffer (pH 5·0) (2 ml) and a 0·1% soln. of eosin or erythrosin are added to a sample soln. of cationic surface-active agent (3×10^{-4} to 3×10^{-3} *M*) (2 ml) and the coloured salt formed is extracted with $CHCl_3$ (5 ml) and determined colorimetrically at 530 mμ after 5 min.

II. Toluidine blue method. Masaru Aoki and Yoji Iwayama. *Ibid.*, 1959, **79** (4), 526–530.—Examination of several kinds of dye as an indicator

for two-phase titration of cationic surface-active agents with anionic surface-active agents showed toluidine blue to be the best. A sample soln. of cationic surface-active agent ($\simeq$ 0·005 *M*) (10 ml) is adjusted to pH 8 with phosphate buffer and titrated with a standard soln. of anionic surface-active agent (0·005 *M*) in the presence of 0·01% toluidine blue soln. (1 ml) and $CHCl_3$ (10 ml). At the end-point the $CHCl_3$ layer changes from crimson to blue; the accuracy is within $\pm$ 0·2%. By the addition of a known amount of a standard soln. of benzalkonium chloride, this method is applicable to the determination of anionic surface-active agents. Toluidine blue is also useful for the colorimetric determination at 650 mμ of anionic surface-active agents in $CHCl_3$. S. NATORI

3370. **Application of gas - liquid chromatography to essential oil analysis. Interim report on the determination of citronellol in admixture with geraniol.** Society for Analytical Chemistry, Essential Oils Sub-Committee of the Analytical Methods Committee. *Analyst*, 1959, **84**, 690–691.—The results of the determination of citronellol in admixture with geraniol by hot formylation, four variants of the original method of Walbaum and Stephan (*Ber.*, 1900, **33**, 2307) being used, were compared with those of determinations by gas - liquid chromatography of the formylated mixtures. The results by the hot formylation method showed considerable divergence from the theoretical composition of the mixture, whereas those obtained by gas - liquid chromatography were near the theoretical content of citronellol. Methods of hot formylation are thus not recommended, and the application of gas - liquid chromatography to the determination of citronellol in essential oils is considered worth further study. A. O. JONES

3371. **Use of flat-headed glass electrodes for measuring the pH of paper.** F. L. Hudson and W. D. Milner (Coll. of Sci. & Technol., Manchester, England). *Svensk Papp-Tidn.*, 1959, **62** (3), 83–84 (in English).—The direct measurement of pH on the moistened surface of paper samples by means of commercial flat-headed glass electrodes gives results which compare well with values obtained by the usual water-extraction techniques. The direct method is rapid and non-destructive.
B. RÖNNHOLM

3372. **Determination of starch in paper: a comparison of the TAPPI, the enzymatic and the spectrophotometric methods.** J. L. Harvey, B. W. Forshee and D. G. Fletcher. *TAPPI*, 1959, **42** (11), 878–883.—A comparison of the TAPPI T419m-45 (*A*), the Brobst and Langlois enzymatic (*B*) and the Browning *et al.* (*C*) methods, with six papers and four starches (corn), showed that none of them is as accurate as desired. Method *A* is the least and *B* the most reproducible. All three methods give high results for small amounts, and low results for high amounts of starch. Method *C*, the only one to give a consistent blank value, is recommended. Whenever possible the same starch as is used in the paper should be used for the calibration curve. R. AICHER

3373. **Determination of chlorine in wood, pulp and paper.** P. O. Bethge and T. Troëng (Forest Products Res. Lab., Stockholm, Sweden). *Svensk Papp-Tidn.*, 1959, **62** (17), 598–601 (in English).—Direct combustion in O followed by potentiometric titration with $AgNO_3$ of the aq. soln. of the combustion products is shown to give better recovery of low chlorine contents than the conventional ashing method. Wood samples are ground to powder and pressed into tablets; paper samples are tightly rolled before burning. The combustion is carried out in a round-bottomed flask (1 litre) with a ground glass stopper. The sample is held by a tungsten spiral attached to the stopper. *Procedure*—Add de-ionised water (10 ml) to the flask. Attach the sample to the tungsten spiral with a small piece of paper of low chlorine content and fill the flask with O. Light the paper, immediately insert the stopper and hold it firmly during the combustion. Cool the flask under the tap, transfer the soln. to a small beaker, add 4 *M* HNO_3 (1 ml), insert a silver - silver chloride electrode and connect to a calomel electrode through a liquid bridge (10% NH_4NO_3 soln.). Titrate with 0·01 *N* $AgNO_3$, with magnetic stirring. Add the titrant in 0·5-ml portions and read the p.d. after each addition, and take 6 to 8 readings after the end-point. Measure the total vol. of the soln., and calculate the results by the method of Gran (*Analyst*, 1952, **77**, 661). Determinations on a sample of bleached sulphite pulp show a coeff. of variation of 4·9%. Results on cellulose and wood samples show chlorine contents from 0·01 to 0·3%. Good recoveries from pulp samples containing known amounts of NaCl are shown. A comparison of results obtained by this method and by conventional alkaline ashing procedures shows that the conventional methods give recoveries of $\gtrsim$ 70%.
B. RÖNNHOLM

3374. **Estimation of tall oil in sulphate black liquor.** W. Saltsman and K. A. Kuiken (Buckeye Cellulose Corp., Memphis, Tenn., U.S.A.). *TAPPI*, 1959, **42** (11), 873–874.—Approx. 800 g of liquor from the centrifugal pumps is diluted to a solids content of 5%. To a 100-ml aliquot in a 500-ml separating-funnel add 5 ml of H_2O_2 [30% H_2O_2 - H_2O (3:2)], 5 ml of 20% Na_2SO_3 soln., 10 ml of HCl (1:1), 200 ml of acetone and 50 ml of ethanol, shaking the mixture between additions. Extract with 150 ml of light petroleum (boiling-range 40° to 60°). Combine the washed light-petroleum extract and the second and third extracts of the aq. phase and evaporate on a water bath. Redissolve the oily residue in 25 ml of light petroleum, filter through a Fisher fritted-glass filter (vacuum type) into a tared evaporating-dish and evaporate. Dry the residue at 105° for 30 min., cool in a desiccator and weigh. Then tall oil (%) on a liquor-solids basis is [wt. (g) of tall-oil residue obtained $\times$ 10]/[wt. (g) of solid in 10 ml of dil. black liquor].
R. AICHER

3375. **Qualitative test for distinguishing tris-(1-aziridinyl)phosphine oxide (APO) and tetrakis-(hydroxymethyl)phosphonium chloride [THPC] [by paper chromatography].** T. D. Miles and A. C. Delasanta (Textile, Clothing and Footwear Div., Res. and Engng Center, Natick, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2051–2052.—Of these two compounds, used as flame-retardants in textile finishes, APO develops a yellow colour at R_F 0·8 and THPC a blue colour at R_F 0·4 when the chromatogram, which has been developed with butanol - 6 *N* HCl (1:4), is treated with ammonium molybdate soln. and exposed to NH_3 fumes. The method is suitable for the analysis of textiles.
G. P. COOK

3376. **Quantitative determination of cotton in cotton - viscose rayon blends.** E. Frieser. *Textil-Praxis*, 1960, **15** (2), 160–168.—Chemical and physical methods for the quant. separation of cotton - viscose rayon blends are reviewed and their accuracies compared. The lowest cotton losses (in wt.) and the most accurate values are obtained by a modified formic acid - $CaCl_2$ method. (28 references.) BRIT. COTT. IND. RES. ASS. ABSTR.

3377. **Complexometric determination of zinc and magnesium in the spinning baths of the viscose industry.** J. Šára and W. Berndt (Spolana n.p. Neratovice, Czechoslovakia). *Faserforsch. u. Textiltech.*, 1959, **10** (11), 541–543.—Accurate works methods are given for determining Zn, Mg and Ca in the spinning baths by titrations with 0·05 *M* EDTA (disodium salt). The presence of Fe has no affect on the result: for any of the metals, and the figures for Ca are not affected by the presence of the other metals. H. L. WHITEHEAD

3378. **Quantitative determination of Rilsan [nylon] in blends with cotton.** G. Gianola and O. Meyer. *Bull. Inst. Text. France*, 1959, (84), 71–76.—The method consists in treating the samples with boiling 98% formic acid for 10 min. to dissolve the nylon component and weighing the remaining cotton after filtering, washing with cold formic acid and water, and drying to constant weight at 105°. Correction factors of 1·02 and 0·98 are used for raw and scoured or bleached cotton, respectively. The method is not applicable to nylon - viscose blends but can be used in the case of nylon - wool blends. BRIT. COTT. IND. RES. ASS. ABSTR.

3379. **Field method for determining moisture in nylon moulding-powder. Steam volumetric method.** N. K. J. Symons and E. C. McKannan (E. I. du Pont de Nemours and Co. Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1990–1993.—The sample is heated in silicone oil in the barrel of a hypodermic syringe; the displacement of the syringe plunger produced by the liberated steam is a linear function of the moisture content, which is calculated from a calibration curve. By choice of convenient sample size, H_2O can be determined in the ranges 0·1 to 1·0 or 1·0 to 10% with standard deviations of $\pm$ 0·035 and 0·35% absolute, respectively. The method appears to be applicable to any sparingly soluble material that is thermally stable up to about 200°. G. P. COOK

3380. **Quantitative analysis of ethylene - propylene copolymers by the mass spectra of their pyrolysates.** E. Bua and P. Manaresi (Soc. Montecatini, Ist. Ricerche Idrocarburi, Ferrara, Italy). *Anal. Chem.*, 1959, **31** (12), 2022–2024.—The method described, which is rapid and gives reproducible results, is based on a standard pyrolysis technique, followed by a mass-spectrometric examination of the volatile products. With the aid of a calibration curve, the copolymer composition can be determined to within about $\pm$ 2%. The accuracy of the method compares well with that of other techniques. K. A. PROCTOR

3381. **Spectroscopic analysis of poly(vinyl chloride) compounds. I. Infra-red spectrometric analysis.** R. A. Burley and W. J. Bennett (Northern Electric Co. Ltd., Wire and Cable Div., Lachine, Quebec, Canada). *Appl. Spectroscopy*, 1960, **14** (2), 32–38.—Resin, plasticiser, stabiliser and filler, in formulations based on poly(vinyl chloride) and poly(vinyl chloride) - poly(vinyl acetate) copolymers, may be quant. estimated by i.r. and emission-spectroscopic procedures, provided chemical separation of the component ingredients is first performed. The plasticiser is obtained by a diethyl ether extraction (*cf.* Haslam *et al.*, *J. Soc. Chem. Ind.*, 1948, **67**, 33; 1950, **69**, 103; *J. Appl. Chem.*, 1951, **1**, 112). The plasticiser (%) is calculated and the i.r spectrum on a sample 0·025 mm thick is obtained, the composition being determined by reference to standard plasticiser spectra. With dioctyl phthalate, CS_2 soln. are used for i.r. spectra determinations. After extraction, the resin is dissolved in tetrachloroethane, the remaining residue is treated with tetrahydrofuran and centrifuged to remove the stabiliser and filler. I.r. spectra of the resin are obtained from films cast on a microscope slide by evaporation of the tetrachloroethane - tetrahydrofuran soln. The stabiliser and filler are examined by KBr pellet or liquid paraffin mull techniques, reserving some sample for a subsequent emission-spectroscopic analysis. These techniques cover a wide formulation range, but further chemical treatment and i.r. examination are required in other cases for a complete analysis. G. P. MITCHELL

3382. **Determination of chlorine in polyurethane plastic.** A. L. Henicksman, E. H. Van Kooten, R. D. Gardner and W. H. Ashley (Los Alamos Sci. Lab., N. Mex.). *U.S. Atomic Energy Comm.*, Rep. LA-2362, Oct., 1959. 11 pp.—Chlorine may be determined in polyurethane by gravimetric or spectrophotometric techniques. The sample is burned in a special combustion tube with two inlets for O, the products of combustion are absorbed in a soln. containing NaOH and H_2O_2, and the chlorine is measured either gravimetrically as AgCl or spectrophotometrically by using mercuric thiocyanate and ferric perchlorate. Eighteen determinations of chlorine in known soln. of sodium chloroacetate or $HClO_4$ gave an average recovery of 98·3% with a coeff. of variation of 2·8%. NUCL. SCI. ABSTR.

3383. **Determination of rosin in protective coating vehicles. I; II.** F. Spagnolo (Nat. Lead Co., Brooklyn, New York). *Paint Varn. Prod.*, 1959, **49** (12), 33–37, 120; (13), 43–50.—A method is proposed for determining the rosin content of alkyd resins containing 0·5 to 5% of rosin. The resin is saponified with KOH in diethylene glycol - phenetole, the unsaponifiable matter is extracted with benzene, the rosin and fatty acids are liberated with H_2SO_4 and extracted with benzene, and the rosin content of the mixed acids is determined by a volumetric selective esterification procedure. The procedure described has been examined and developed as an ASTM tentative method. L. A. O'NEILL

3384. **Complexometric determination of the total zinc and zinc oxide content of lithopone.** A. Schaller and E. Mihalovics (Bundeslehr- u. Versuchsanst. f. Chem. Ind., Wien). *Öst. ChemZtg*, 1959, **60** (12), 338–344.—For the determination of the total Zn, the sample (0·2 to 0·4 g) is heated with 4 *N* HCl (25 ml) until evolution of H_2S ceases, and then with a few drops of conc. HNO_3. After dilution, 2 *N* H_2SO_4 (5 ml) is added, and if required the $BaSO_4$ content may be determined gravimetrically. The Zn content of the soln., with or without removal of the $BaSO_4$, is then determined by titration with 0·01 *N* EDTA (disodium salt), with Eriochrome black T as indicator, in the presence of NH_4F and an

aq. NH_3 - NH_4Cl buffer soln. (pH 10). The ZnO content is determined by extracting the sample with the buffer soln., centrifuging off the clear soln. and determining its Zn content complexometrically. The results are slightly high on account of interference by traces of Mg and alkaline-earth-metal oxides. L. A. O'NEILL

3385. **Colorimetric determination of diethyl, dibutyl and dioctyl phthalates in ball propellents.** G. Norwitz (Frankford Arsenal, Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2012–2015.—The phthalate is extracted from the propellent with diethyl ether and the nitroglycerin and dinitrotoluene in the extract are reduced with $TiCl_3$ in buffered acetate medium. The phthalate is extracted into light petroleum, which is evaporated off, and the residue is converted into a hydroxamic acid by treatment with hydroxylamine and NaOH, and then into a coloured complex by the addition of ferric perchlorate. The extinction is measured at 650 mμ to eliminate interference from 2-nitrodiphenylamine at the max. absorption of 540 mμ. The standard deviation was ± 0·086%, and the mean result 4·82%, on a sample containing 4·95% of dibutyl phthalate (7 analyses). G. P. COOK

3386. **Identification of high explosives by microscopic fusion methods.** W. C. McCrone (Dept. of Chem., Cornell Univ., Ithaca, New York, U.S.A.). *Microchem. J.*, 1959, **3** (4), 479–490.—Data are given for the microscopic identification of individual members of a group of 27 compounds used as high explosives. The compound is classified as belonging to one of 7 groups on the basis of a mixed fusion with thymol, and final identification is obtained by the observation of the melting-point of the pure compound and its crystal habit. W. T. CARTER

See also Abstracts—**3105**, Automation in petroleum analysis. **3129**, Tritium in org. compounds. **3198**, Polarography of hydroxamic acids. **3242**, Chloride in sulphite waste liquor. **3417**, Separation of *p*-benzoquinones.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

3387. **Standardisation of clinical-chemical methods.** A. H. Holtz (Rijksinst. v. d. Volksgezondheid, Utrecht, Netherlands). *Chem. Weekbl.*, 1959, **55** (43), 590–591.—The Dutch committee on the standardisation of clinical-chemical methods has published a standard procedure for the determination of urea in blood, plasma and serum. The method is based on the conversion of urea into ammonium carbonate with urease at pH 7.
M. J. MAURICE

3388. **Fluorimetric estimation of magnesium in serum and urine.** D. Schachter (Columbia Univ., New York, U.S.A.). *J. Lab. Clin. Med.*, 1959, **54** (5), 763–768.—The method described requires 0·1 ml of serum or 0·2 ml of diluted (1:4) urine and is based on the difference in the fluorescence of magnesium 8-hydroxyquinolinate in aq. ethanolic acetate buffers at pH 3·5 and 6·5. The calibration graph is rectilinear up to 0·2 milli-equiv. per litre and Ca^{2+} do not interfere. The fluorescence is measured at 530 mμ with activation at 420 mμ.
W. H. C. SHAW

3389. **Estimation of "free" calcium in urine and its relevance to calculus formation.** B. E. C. Nordin and A. Bell (Univ. Dept. of Med., Gardiner Inst., Western Infirmary, Glasgow). *Brit. J. Urol.*, 1959, **31** (4), 404–413.—It is postulated that the calcium in urine is present partly in the "bound" form, as citrate, etc., and partly in the "free" form. A method for the determination of the "free" fraction is described, based on the fact that the addition of alkali to inorganic soln. of calcium and phosphate results in the appearance of a ppt. [probably $Ca_3(PO_4)_2$], and the pH at which the ppt. appears is inversely related to the product of the concn. of calcium and phosphate. The urine, acidified with a few drops of HCl and filtered if not absolutely clear, is placed in a vessel illuminated from the side and 0·1 *N* NaOH is added until the white ppt. formed does not re-dissolve on stirring. The pH is then measured with a glass-electrode pH meter; from this reading the amount of "free" calcium is determined by means of a nomogram.
R. A. BRENAN

3390. **Flame-photometric determination of calcium in blood plasma or in protein solutions containing phosphate.** H. Glasmacher (Physiol.-Chem. Inst. u. Augenklinik, Univ. Bonn, Germany). *Arzneimittel-Forsch.*, 1959, **9** (11), 671–672.—The Ca content of blood plasma or of protein soln. containing phosphate, as determined by flame photometry, increased on storage. The apparent increase in Ca content was more pronounced at higher temp. Plasma samples should be analysed within 2 hr.
A. G. COOPER

3391. **Measurement of ammonia in plasma and blood.** J. A. Jacquez, R. Jeltsch and M. Hood (Sloan-Kettering Inst., New York, U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (6), 942–954.—A kinetic study is made of the rate of diffusion of NH_3 from standards, blood and plasma in the Conway microdiffusion method. It is concluded that diffusion from standards with time follows an exponential curve, but from blood and plasma the linear portion of the curve exhibits a slope depending on the rate of formation of NH_3 in the samples. Highest accuracy is attained by plotting several points on the linear portion and extrapolating to zero time. The proteins in plasma and blood are shown to be the major precursors from which NH_3 is formed under alkaline conditions. W. H. C. SHAW

3392. **Micro-determination of phosphate in the range of 1 to 10 micrograms.** A. A. Hirata and D. Appleman (Coll. of Agric., Calif. Univ., Los Angeles, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2097–2099.—The Bernhart and Wreath method (*Anal. Abstr.*, 1955, **2**, 2078) has been modified to ensure a 15-fold increase in sensitivity and thus to provide for the determination of 1 to 10 μg of P in a biological sample. *Procedure*—To tissue extract (2 to 4 ml) in a silica tube add 70% $HClO_4$ (0·33 to 0·66 ml) and heat at 203° for 40 min. Transfer the soln. to a 10-ml flask, add ammonium molybdate reagent (2 ml) and mix well, then add acetone (4 ml, measured at 0°) and make up to the mark with H_2O. Mix thoroughly and measure the extinction of the molybdophosphate complex at 320 mμ and 20° to 25° against a reagent blank. The concn. of

acetone must always be 30 to 40% (v/v) and that of $HClO_4$ 0·35 to 0·70 *N*. The precision is within 0·3%, and the method has been successfully applied to plant mitochrondria and to *Tetrahymena* and *Chlorella*. W. J. BAKER

3393. **Determination of phosphorus in very small quantities of serum. Ultra-micro modification of the method of Fiske and Subbarow using amidol [2:4-diaminophenol hydrochloride].** H. Doose (Univ.-Kinderklin., Kiel). *Z. ges. exp. Med.*, 1959, **131**, 646–648.—The method is applicable to 0·05 ml of serum. NUTR. ABSTR. REV.

3394. **Detection of antimony in biological materials by fractional analysis.** A. N. Krŷlova. *Sudebno-Med. Ekspertiza*, 1959, **2** (3), 31–36; *Ref. Zhur., Khim.*, 1960, (3), Abstr. No. 8916.—The detection is based on the production of a coloured complex from antimony and malachite green. To eliminate interference from Fe, the reaction is carried out in 40 to 50% H_2SO_4 in the presence of Na_2SO_4, and toluene is used to extract the coloured complex. Alternatively, the thiosulphate complex of antimony is heated to give an orange - yellow ppt. of antimony sulphide. K. R. C.

3395. **Micro-determination of selenium in biological materials.** R. Handley and C. M. Johnson (Univ. of California, Berkeley, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2105–2106.—From 0·25 to 10 μg of Se in, *e.g.*, plant tissue, can be determined by a modification of Cheng's method (*cf. Anal. Abstr.*, 1957, **4**, 1189), in which the yellow Se^{IV} - 3:3′-diaminobenzidine complex (**I**) is used. The dried sample (1 g, 40 mesh) is digested for 2 to 3 hr. with a mixture of HNO_3, H_2SO_4 and $HClO_4$, and the soln. is then distilled with a mixture of HBr and Br, the vol. of distillate (containing $SeBr_4$) being kept small. An air condenser, and a stream of N passing through the apparatus, ensure a min. concn. of HBr in the distillate. After destroying residual Br with phenol and adjusting the pH to ≃ 7 with aq. NH_3, conc. formic acid is added dropwise to the distillate until the pH is 2·5, and 0·5% aq. 3:3′-diaminobenzidine hydrochloride soln. (2 ml) is then added. After 1 hr. the pH is again adjusted to 7 with dil. aq. NH_3, and **I** is extracted from the soln. with toluene (1 ml). The extract is centrifuged and the extinction of the clear soln. is measured immediately at 420 mμ in a 0·7-ml cell at 25°. Values are slightly low in the range of 0 to 5 μg of Se, and calibration curves are necessary. W. J. BAKER

3396. **Colorimetric determination of selenium in biological materials.** C. W. Bonhorst and J. J. Mattice (Portland Univ., Ore., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2106–2107.—A procedure is given for determining Se, to within 0·2 μg, in dry material (10 g) or wet tissue, milk or blood (30 to 50 g). The sample is digested with a mixture of HNO_3 (25 ml) and H_2SO_4 (25 ml) containing HgO (0·1 g); conc. HCl (25 ml) is then added to obviate interference by Fe and SO_4^{2-}, and the cool soln. is saturated with SO_2. Hydroxyammonium chloride (1 g) is added and the warm soln. is set aside for 48 hr. before filtration through a 12-mm filter-tube. The flask is rinsed with Br soln. and after removal of residual Br (in rinsings) from the filtrate with phenol, the Se^{4+} are determined spectrophotometrically by Cheng's method (*cf. Anal. Abstr.*, 1957, **4**, 1189). The 3:3′-diaminobenzidine used should be prepared by the method of Hoste (*Anal. Chim. Acta*, 1948, **2**, 402). W. J. BAKER

3397. **Estimation of small amounts of fluoride in body fluids.** H. W. Linde (Ohio Chem. and Surgical Equipment Co., Air Reduction Co., Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2092–2094.—From 0·1 to 0·5 μg of F^- per ml of body fluid or water can be determined directly by measuring their inhibitory effect on the hydrolysis of ethyl *n*-butyrate by liver lipase at 25°. The butyric acid formed is titrated potentiometrically to pH 7·7, in ethanolic soln., with 0·05 *N* NaOH, against a reagent blank. The percentage hydrolysis is inversely proportional to log (concn. of F^-). The reproducibility (0·1 to 0·2 μg) is less than that of the Singer and Armstrong procedure (*Anal. Abstr.*, 1959, **6**, 3092), but the sensitivity is ≃ 0·1 μg per ml for blood and urine and ≃ 0·1 μg per 100 ml for water. Ashing the sample is not necessary, so that the method is applicable in the presence of organic compounds containing non-labile F atoms. There is interference in the presence of substances that affect enzyme activity or hydrolysis of the ester, or that are excessively buffered. W. J. BAKER

3398. **Rapid method for determination of liquid-bound radio-iodine in blood.** H. D. Strauss and H. K. Richards (Veterans Admin. Hosp., Philadelphia, Pa., U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1959, **100**, 461–463.—*Procedure*—Add 2 ml of water to 2 ml of heparinised whole blood in a test-tube. Set aside for 5 min. to allow haemolysis to occur. Pass through an ion-exchange column (Rezekit), wash the column twice with 1-ml portions of isotonic saline soln. and add the washings to the eluate. Count the eluate for ^{131}I in a well-type scintillation counter. B. P. BLOCK

3399. **Micro-method for serum-iron determination.** C. W. Woodruff (Vanderbilt Univ., Nashville, Tenn., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (6), 955–957.—A modification of the method of Ramsay (*Biochem. J.*, 1953, **53**, 227) is described. *Procedure*—To 60 μl of serum in a test-tube (6 mm × 50 mm) add 100 μl of Fe-free water, 40 μl of 0·1 *M* Na_2SO_3 and 40 μl of 0·5% 2:2′-dipyridyl soln. in 0·5 *M* acetate buffer, pH 4·0. Mix thoroughly, allow to stand at room temp. for 30 min. then place in boiling water for 3 min. Shake, continue heating for a further 2 min. and allow to stand for 12 to 24 hr. Separate the coagulated proteins by centrifugation and determine the extinction of the supernatant liquid in ultra-micro cells at 510 mμ. Standards contain 20 to 500 μg of Fe per 100 ml. The standard deviation between duplicates is 3·8 μg per 100 ml, and recovery of added Fe is 99·0 ± 1·3%. W. H. C. SHAW

3400. **Rapid determination of mixed β-γ radionuclides in urine.** A. L. Boni (E. I. du Pont de Nemours & Co., Aiken, S.C., U.S.A.). *Health Phys.*, 1959, **2**, 186–188.—A bioassay procedure was developed which makes possible the rapid determination of the total amount of β-γ-emitting isotopes in a specimen of urine. The β-γ-emitting radionuclides are co-pptd. from urine on an alkaline-earth-metal phosphate ppt. The separated ppt. is ignited, dissolved and directly plancheted. The planchet is both β- and γ-counted. The recoveries of ^{89}Sr, ^{90}Sr - ^{90}Y, ^{95}Zr - ^{95}Nb, ^{144}Ce - ^{144}Pr, ^{59}Fe, ^{51}Cr and ^{65}Zn are > 90%. The recovery of Co is 85%. NUCL. SCI. ABSTR.

3401. **Simple fluorimetric procedure for determining salicylic acid in biological tissues.** M. A. Chirigos and S. Udenfriend (Nat. Heart Inst.,

Bethesda, Md., U.S.A.). *J. Lab. Clin. Med.*, 1959, **54** (5), 769–772.—Prepared tissue homogenates or diluted plasma samples are acidified and extracted with diethyl ether. The ether is separated by centrifugation and an aliquot is re-extracted with borate buffer (pH 10). Dissolved ether is evaporated from the buffer soln. and the fluorescence is then measured at 400 mμ with activation at 310 mμ. Quant. recovery of salicylic acid is attained and blanks on the tissues studied were negligible. The calibration graph is rectilinear up to 2 μg per ml of fluorescent solution. W. H. C. SHAW

3402. **Improved colorimetric method for the determination of meprobamate in biological fluids.** A. J. Hoffman and B. J. Ludwig (Wallace Lab., Div. of Carter Products Inc., New Brunswick, N.J.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (12), 740–742.—The method described previously (Ludwig and Hoffman, *Anal. Abstr.*, 1958, **5**, 2317) has been simplified and improved. *Procedure*—Vigorously shake the sample of plasma, serum or spinal fluid (1 ml) with 28% aq. NH_3 (2 drops), satd. aq. KCl soln. (2 drops) and $CHCl_3$ - CCl_4 (1:1) (25 ml) for 5 min., then centrifuge for 10 min. Evaporate the organic layer to dryness at 80°, add acetone - glacial acetic acid (3:1) (0·2 ml) followed by a 1% soln. of *p*-dimethylaminobenzaldehyde in benzene (0·2 ml) and mix. Add a mixture of acetic anhydride and a satd. soln. of $SbCl_3$ in $CHCl_3$ (1:4) (0·2 ml), mix and heat at 50° in a stoppered tube for exactly 10 min. Cool rapidly, add benzene (1 ml) and measure the extinction at 550 mμ against a blank prepared by similar treatment of H_2O (1 ml). The extinction is directly proportional to the concn. of meprobamate in the range 0·5 to 10 μg per ml. The coeff. of variation is $\simeq \pm 4\%$. Urea and other substances interfere with the determination in urine and must be destroyed by heating the extract for 15 min. at 50° with HCl before the colour development. A. R. ROGERS

3403. **Separation and quantitative estimation of sulphanilamide and allied drugs in blood and urine by paper chromatography.** A. Sinha (Chem. Lab., Dept. of Pharmacol., Med. College, Agra). *J. Instn Chem., India*, 1959, **31** (6), 282–284.—Remove protein from samples of blood; filter samples of urine. Clarify by centrifugation, add aq. NaOH soln. and apply an aliquot to Whatman No. 1 paper. Develop with *n*-butanol - acetic acid - H_2O (5:1:4) or *iso*butyl alcohol - ethanol - H_2O (4:1:4) at 25° in the vapour of phenol-saturated aq. NH_3; dry the chromatogram at 60° for 30 min., spray with Ehrlich's reagent, elute the dried spots and determine colorimetrically. R_F values are given for sulphanilamide, sulphapyridine, sulphathiazole, sulphadiazine and sulphamerazine in the two solvent systems. A. R. ROGERS

3404. **Photometric determination of *iso*nicotinic acid hydrazide [isoniazid], its derivatives and their metabolites in biological specimens. II.** W. Nielsch and L. Giefer (Joh. A. Benckiser G.m.b.H., Ludwigshafen). *Arzneimittel-Forsch.*, 1959, **9** (11), 700–707.—Methods for the determination of isoniazid (**I**) are reviewed. Colorimetric procedures for the determination of *iso*nicotinic acid (**II**) and *iso*nicotinoylglycine (**III**) in plasma and in urine are described, comprising reaction with CNCl (generated *in situ* from KCN and chloramine T) and condensation of the glutaconic dialdehyde so obtained with barbituric acid at pH 5. The extinction of the resulting polymethine dye is read at 600 mμ (for **II**) and at 615 mμ (for **III**). **I** and its metabolites (**IV**) do not interfere. To determine the total quantity of **I** plus **IV**, an aliquot is subjected to alkaline hydrolysis to convert **I** and **IV** into **II**. To determine **I** and **IV** separately, an aliquot is treated with HNO_2 to convert **I** and **IV** into **II**. Conversion of **I** in a second aliquot into **II** on treatment with HNO_2 is prevented by prior reaction with acetic anhydride to yield the N′-acetyl derivative. A paper-chromatographic test for the detection of **I** and **IV** in urine and in plasma is described, comprising spraying with barbituric acid soln. and exposure to humid CNCl vapour. The method will detect 0·01 μg of **II**. A. G. COOPER

3405. **Contributions to the detection and quantitative determination of 2:3-dimethyl-1-phenyl-4-pyrrolidino-5-pyrazolone in serum and medicinal solutions.** W. Strunz (Wien XVII, Dornbacherstrasse 86/6). *Sci. Pharm.*, 1959, **27** (3), 145–148.—To distinguish 2:3-dimethyl-1-phenyl-4-pyrrolidino-5-pyrazolone (**I**) from amidopyrine, phenazone and 4-aminophenazone, use the colour reactions with $K_3Fe(CN)_6$, aq. NH_3, $FeCl_3$, H_2SO_4 - $K_2Cr_2O_7$, chloral hydrate and $NaNO_2$ soln. To determine **I** in serum, remove proteins by pptn. with hot acetate buffer soln., render the soln. alkaline with 2 *N* NaOH, extract with diethyl ether and evaporate the ether layer to dryness. Allow the extracted **I** to react with cyanogen bromide soln., couple with diazotised *p*-nitroaniline and measure the extinction of the dye extracted with $CHCl_3$, with filter S43; Beer's law is obyed in the range of concn. 0·5 to 6 mg per 100 ml and the mean error is $\simeq \pm 4\%$. To determine **I** in medicinal soln., heat the sample (5 ml containing 15 mg of **I**) under reflux for 1 hr. with aq. H_2SO_4 (1:1) (10 ml) and 2% $K_2Cr_2O_7$ soln. (10 ml), cool, add 10% NaI soln. (10 ml), dilute to 100 ml, titrate with 0·1 *N* $Na_2S_2O_3$ soln. until the colour is only a pale yellow - green, dilute to 500 ml and complete the titration, with starch as indicator. A. R. ROGERS

3406. **Psicofuranine. VII. Chemical determination in plasma and serum.** A. A. Forist, S. Theal and H. Hoeksema (Res. Lab., The Upjohn Co., Kalamazoo, Mich., U.S.A.). *Antibiot. & Chemother.*, 1959, **9** (11), 685–689.—Mix the sample (1 ml) with abs. ethanol (4 ml), set aside for 30 min., centrifuge, and evaporate a 3-ml aliquot of the supernatant liquid to dryness. Mix the residue with a fresh 5% soln. of $NaBH_4$ in 0·1 *N* NaOH (0·5 ml) and set aside for 1 hr. Cautiously add 2 *N* HCl (0·5 ml) and diphenylamine reagent [dissolve diphenylamine (10 g) in glacial acetic acid (500 ml) and dilute to 1 litre with conc. HCl] (2 ml). Heat in boiling water for 1 hr., cool, centrifuge, and measure the extinction of the clear soln. at 630 mμ against a reagent blank. Treat similarly a sample of plasma or serum obtained from the same subject before the administration of the psicofuranine. Recovery experiments show that the mean deviation is $\simeq 2{\cdot}5$ μg per ml over the range 20 to 100 μg per ml. The results agree with those of microbiological and radioactive tracer assays. A. R. ROGERS

3407. **Determination of glycols by polarography. II. Determination of blood sugar.** Kiyoshi Takiura and Kyoko Koizumi (Pharm. Fac., Osaka Univ., Toyonaka-shi). *J. Pharm. Soc. Japan*, 1959, **79** (6), 809–814.—The polarographic determination of glycols by the use of KIO_4 (*Anal. Abstr.*, 1960, **7**, 1061) was applied to the determination of blood sugar. The plasma soln. is prepared by adding

isotonic or slightly hypertonic phosphate buffer (pH 7·0) to blood and centrifuging the blood corpuscles. The soln. (1 ml, corresponding to 0·1 ml of blood) is mixed with KIO_4 - Sørensen buffer soln. (10 ml, 10^{-3} *M*, pH 7·0) and maintained at 25° ± 0·1° for a known time (0·5 to 2 hr.), and the wave height of the first polarographic wave of IO_4^- is measured. Comparison of this method with Hagedorn and Jensen's method and the anthrone method was made with normal blood and with blood after administration of glucose, insulin or adrenaline; similar results were obtained. Deproteinisation is not needed in this method, and the reaction is stoicheiometric so that it is not necessary to use an empirical factor. S. NATORI

3408. **Diagnostic compositions [for the detection and estimation of glucose in urine and other body fluids].** Miles Laboratories, Inc. Brit. Pat. 831,804, date appl. 5.11.56; U.S.A., date appl. 3.2.56.—The compositions contain (*i*) glucose oxidase, (*ii*) blood, red blood cells, lyophilised whole blood or blood cells or mixtures of lyophilised blood and plasma, (*iii*) an indicator which undergoes a colour reaction in the presence of hydrogen peroxide and a member of group (*ii*), *e.g.*, *o*-tolidine dihydrochloride, and (*iv*) a citrate buffer for maintaining the pH of the mixture at ≃ 5·4 in the presence of urine. The basic principle of the test is the fact that, in an aerobic system in the presence of glucose oxidase, glucose is oxidised to gluconic acid and hydrogen peroxide. This reaction is highly specific for glucose, and other sugars are oxidised only to an insignificant extent. The compositions can be prepared in powder or tablet form, or as suspensions or soln. for impregnating paper. J. M. JACOBS

3409. **Determination of polysaccharide hexoses and hexosamines in normal human sera.** G. Höxter, B. L. Wajchenberg, I. Martirani and A. B. V. Cintra (São Paulo Univ., Brazil). *J. Lab. Clin. Med.*, 1959, **54** (5), 773–778.—A study is presented of methods for the determination of total glycoprotein and $HClO_4$-soluble seromucoid hexoses in normal sera. A method requiring an anthrone reagent modified by the addition of H_3BO_3 is considered to be the most satisfactory and of high specificity. Results for the two types of hexose derivatives are in agreement with accepted values. W. H. C. SHAW

3410. **Partition chromatography of homologous saccharides on cellulose columns.** J. A. Thoma, H. B. Wright and D. French (Iowa State Coll., Ames, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **85** (2), 452–460.—Chromatography of 1 to 2·5 g of starch and inulin hydrolysates is carried out at 53° on cellulose-powder columns; elution is with mixtures of water, ethanol and *n*-butanol, the water content being increased stepwise during elution. Separation of homologous saccharides of up to 20 monosaccharide units is attained. W. H. C. SHAW

3411. **Rapid photometric method of determining urea in body fluids.** R. Delcourt (Serv. Pathol. Clin., Hôp. Ixelles). *Rev. Belge Path.*, 1959, **27**, 50–60.—To plasma or serum (1 ml) were added successively water (1 ml), 4% *p*-dimethylaminobenzaldehyde soln. in 94% ethanol (0·5 ml) and 10% trichloroacetic acid soln. in *N* HCl (2 ml). After 10 min. the mixture was centrifuged and the extinction was measured at 430 and 475 mμ. For blood or urine containing sulphonamides, duplicate tubes were first treated with urease or water for 30 min. Results were similar to those obtained by a gasometric method with hypobromite. NUTR. ABSTR. REV.

3412. **Detection and identification of deoxy sugars on paper chromatograms.** A. P. MacLennan, H. M. Randall and D. W. Smith (Univ. Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2020–2022.—A mixture of vanillin with $HClO_4$ or H_2SO_4 reacts with deoxy sugars on paper chromatograms to form coloured products. Several classes of deoxy sugars give highly distinctive colours, which assist in the identification of deoxy sugars that belong to different classes but have similar *R* values. Data for about 30 sugars are listed. G. P. COOK

3413. **Studies on the determination of glucuronic acid. II. The separate determination of glucuronic acid and glucuronides by ion-exchange resin.** Morizo Ishidate, Shoji Takitani and Terumi Nakajima (Fac. of Pharm. Sci., Tokyo Univ.). *J. Pharm. Soc. Japan*, 1959, **79** (6), 843–845.—A mixture of glucuronic acid (**I**), phenylglucosiduronic acid (**II**), methylglucosiduronic acid (**III**) and Na anilino-N-glucosiduronate (**IV**) was passed through a column of Amberlite IRA-411 (R-Cl type, 5 ml) in weakly basic state and elution of the column with *N* HCl afforded **I** and an N-glucuronide (of **IV**). Further elution with a mixture of HCl and methanol (11:25) gave O-glucuronides (of **II** and **III**). The determination of glucuronic acid in each fraction was made by the carbazole method. A test with urine showed 93·9 to 101·5% recovery. S. NATORI

3414. **N-Glucuronides of sulphonamides. I. Separate determination of a mixture of the N-glucuronides of sulphonamides and other glucuronic acid conjugates.** Shōzaburō Ōgiya and Hideo Kataoka (Tohoku Coll. of Pharm., Odawara, Haranomachi, Sendai). *J. Pharm. Soc. Japan*, 1959, **79** (7), 949–953.—A process for the separate determination of glucuronic acid (**I**), ester-conjugated glucuronides (**II**), ether-conjugated glucuronides (**III**), and N-glucuronides (**IV**) was examined. Total glucuronic acid (**I** + **II** + **III** + **IV**) is determined by Ishidate and Nambara's method (*Pharm. Bull., Japan*, 1957, **5**, 515). Reduction with $NaBH_4$ gives the amount of **II** + **III** + **IV**, hydrolysis with NaOH gives **III** + **IV** and oxidation with NaOBr gives **III**. Conditions for the determination of the glucuronides in urine are examined. S. NATORI

3415. **Determination of heparin in blood.** E. Hiepler (Wissenschaft. Abt., Dtsch. Hoffmann-La Roche A.-G., Grenzach). *Arzneimittel-Forsch.*, 1959, **9** (12), 763–765.—Dilute 0·2 ml of a heparin preparation ("Liquemin") with 4·8 ml of 0·9% NaCl soln., and dilute 0·5 ml of this mixture with 9·5 ml of 0·9% NaCl soln. to obtain a soln. containing 100 μg of heparin per ml. Dilute further with water to obtain standard soln. (*A*) containing 2·5, 5, 7·5, 10, 12·5, 15 and 20 μg of heparin per ml. Prepare a 5% soln. (*B*) of thromboplastin by dilution of 0·2 ml of thromboplastin soln. (Roche) with 3·8 ml of 0·9% NaCl soln., add 40 mg of fibrinogen and store on ice. Mix 9 parts of citrated blood (9 parts of blood to 1 part of 3·6% citrate soln.) with 1 part of 0·9% NaCl soln. and haemolyse 0·1 ml of the mixture for 10 min. at room temp. with 0·4 ml of *A*. Warm for 1 min. at 37°, add 0·1 ml of 0·025 *M* $CaCl_2$, add 0·1 ml of *B* and determine the coagulation time by the

platinum-hook method. Prepare a standard curve to determine the original heparin content of the blood. A. G. COOPER

3416. **Spectrophotometric determination of thioctic acid.** M. Covello and C. de Vena (Naples Univ.). *Ric. Sci.*, 1959, **29** (12), 2552–2560.—Thioctic acid (6:8-dithio-octanoic acid) is reduced with zinc and NaOH soln., then acidified, and the H_2S is distilled and collected in alkaline Zn acetate soln. The ZnS formed is treated with *p*-amino-NN-dimethylaniline and the S present is converted quant. by oxidation with $FeCl_3$ into methylene blue, which is determined spectrophotometrically at 665 mμ. The method has been used successfully for the determination of thioctic acid in urine. L. A. O'NEILL

3417. **Separation of naturally occurring *p*-benzoquinones by chromatoplates.** M. Barbier (Inst. de Biologie Phys.-chim., Paris, France). *J. Chromatography*, 1959, **2** (6), 649–651 (in French).—The chromatographic separation of *p*-benzoquinones, occurring in plant and animal secretions, on plates of silicic acid, is described. G. S. ROBERTS

3418. **Polarography of gibberellic acid.** W. F. Head, jun. (Anal. Res. Dept., Eli Lilly and Co., Indianapolis, Ind.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (11), 631–634.—The polarographic characteristics of several gibberellins have been determined. Gibberellic acid (**I**) possesses a characteristic pre-wave at −1·0 to −1·2 V *vs.* the S.C.E. in addition to a larger wave at −1·55 V shown by all gibberellins. To determine **I** in tablets and powders, extract the sample with *iso*butyl methyl ketone, evaporate the extract to dryness, dissolve the residue in 0·1 *N* KCl and measure the pre-wave current, which is proportional to the concn. of **I** in the range 100 to 600 μg per ml. The average recovery is 97%; the accuracy is ± 2%. Sodium lauryl sulphate and some dyes may interfere. A. R. ROGERS

3419. **Determination of chlorophylls *a* and *b* by paper chromatography.** D. I. Sapozhnikov, A. N. Maevskaya and I. A. Popova. *Fiziol. Rastenil, Akad. Nauk SSSR*, 1959, **6** (3), 376–379; *Ref. Zhur., Khim., Biol. Khim.*, 1959, (24), Abstr. No. 31,702.—*Procedure*—Fix the sample of leaves (1 to 2 g) with acetone at −78°, grind them in acetone - 96% ethanol (3:1) with a small amount of alkali and sand, filter off the solid matter, wash it with the same solvent mixture and dilute the extract to 25 ml. Apply the soln. (1 to 2 ml) to filter-paper contained in a jar with a ground glass stopper and run an ascending chromatogram for 20 to 30 min. with light petroleum - ethanol (20:1 or 40:3). Recover the chlorophylls *a* and *b* from the pigment zones by means of small amounts of diethyl ether; wash with acetone - ethanol and determine the extinction of 10 ml. It is shown that chlorophyllides in the extract remain at the point of application and their extinctions therefore do not affect those of the chlorophylls. The error is ≯ 4%. K. R. C.

3420. **The chromatography of the flavonoid pigments.** J. B. Harborne (John Innes Hort. Inst., Hertford, England). *J. Chromatography*, 1959, **2** (6), 581–604 (in English).—A review, with 91 references. G. S. ROBERTS

3421. **Quantitative determination of flavanones in citrus bioflavonoids by potassium borohydride reduction.** K. M. Rowell and D. H. Winter (Orange Products Div., Sunkist Growers, Ontario, Calif.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (12), 746–749.—Dissolve KBH_4 (50 mg) in a soln. of hesperidin (**I**) (≃ 500 μg), hesperetin (**II**) (≃ 125 μg), naringin (**III**) (≃ 125 μg) or naringenin (**IV**) (≃ 60 μg) in aq. NaOH soln. (5 ml) and then add 0·5 *N* acetic acid (5 ml) dropwise during 4 min. Mix a 1-ml aliquot of the reduced material with a 5% soln. of conc. HCl in glacial acetic acid (5 ml), set aside for 30 min. (5 min. for **II**; 18 min. for **I**) at 20° and measure the extinction at 560 mμ (for **I**), 540 mμ (**II**), 552 mμ (**III**) or 535 mμ (**IV**). Use as blank a mixture of the reduced material (1 ml) and glacial acetic acid (5 ml) prepared just before the measurement. The coeff. of variation is ≃ ± 0·5%. The method has been adapted to the determination of flavanones in pharmaceutical preparations. A. R. ROGERS

3422. **Analysis of compounds containing heavy nitrogen (nitrogen-15) by infra-red absorption spectra.** Goro Chihara and Keiichi Tanikawa (Div. of Biochem., Central Clin. Lab., Tokyo Univ. Hospital). *Chem. & Pharm. Bull., Japan*, 1959, **7** (8), 920–924 (in English).—Ammonia is liberated by a Kjeldahl technique and the i.r. absorption is measured in a 20-cm cell. As little as 0·1 mg of ^{15}N can be detected by the absorption band at 863·6 cm^{-1}. The ratio of ^{15}N to ^{14}N can be estimated from the ratio of the extinctions at 863·6 and 872·5 cm^{-1}. The technique is simpler than that of mass spectrometry, but a larger sample is needed and the precision is less. A. R. ROGERS

3423. **Determination of urinary hexosamine.** G. Margotte-Boy, R. Henry and R. Issartel (Lab. de Biochim. Méd., Prof. M. F. Jayle, 45 rue Saints-Pères, Paris, France). *Bull. Soc. Chim. Biol.*, 1959, **41** (11), 1485–1496.—Various methods for determining urinary hexosamine have been examined and compared. A modified technique is proposed in which three fractions are isolated, (*i*) by dialysis, (*ii*) by pptn. with ethanol and (*iii*) by pptn. with $CaCl_2$ from the supernatant liquid from (*ii*). The ppt. are hydrolysed with 3 *N* HCl on a boiling-water bath for 7 hr. and the hexosamine is determined colorimetrically by reaction with acetylacetone and *p*-dimethylbenzaldehyde. The sum of the hexosamine in these fractions equals the total hexosamine determined directly in urine. S. M. MARSH

3424. **Fluorimetric assay of histamine in tissues.** P. A. Shore, A. Burkhalter and V. H. Cohn (Nat. Heart Inst., Bethesda, Md., U.S.A.). *J. Pharmacol.*, 1959, **127**, 182–186.—The method involves extraction of histamine into *n*-butanol from alkalised $HClO_4$ extracts of tissues, return to an aq. phase and condensation with phthalaldehyde to form a highly fluorescent compound which is determined in a spectrofluorimeter (activation at 360 mμ, fluorescence at 450 mμ). Concn. of histamine as low as 0·005 μg per ml can be determined. CHEM. ABSTR.

3425. **Method for determining xanthurenic acid after fractionation of urine by high-tension electrophoresis.** R. Clotten and A. Clotten (Med. Klin., Univ. Freiberg i. Br.). *Z. ges. exp. Med.*, 1959, **131**, 379–395.—In the first method the paper is sprayed with an alkaline soln. of diazotised sulphanilic acid; the resulting dark-red spot is eluted with water and the extinction is measured at 500 mμ. The method is not completely reliable, owing to the instability of the diazo reagent, and a second procedure, depending on the green colour given by

xanthurenic acid and $(NH_4)_2SO_4.Fe_2(SO_4)_3$, was developed. The paper is sprayed with the reagent and then with a tri(hydroxymethyl)methylamine buffer (pH 7·8), to increase the specificity of the reaction. The coloured complex is eluted with the same buffer and its extinction is measured at 620 mμ.

NUTR. ABSTR. REV.

3426. **Identification and assay of urinary tryptamine: application as an index of mono amine oxidase inhibition in man.** A. Sjoerdsma, J. A. Oates, P. Zaltzman and S. Udenfriend (Sect. Exp. Therap., Nat. Heart Inst., Nat. Inst. Health, Bethesda, Md.). *J. Pharmacol.*, 1959, **126**, 217–222.—Urine (15 ml) at a pH > 11 was shaken for 20 min. with benzene (30 ml) and then centrifuged. The benzene layer was washed with 0·1 *N* NaOH (2 × 5 ml) and, after centrifuging, 25 ml of the soln. was shaken with 0·7 ml of 0·1 *N* HCl for 15 min., and then centrifuged. A portion of the acid soln. (0·5 ml) was mixed with 0·13 *M* borate buffer (pH 10) (1 ml), and the tryptamine was measured spectrophotofluorimetrically, at 285 mμ for activation and at 360 mμ for fluorescence. The final extract contained a constant 40% of the original tryptamine. Fluorimetric methods of identification are also described. NUTR. ABSTR. REV.

3427. **Colorimetric estimation of α-amino nitrogen in tissue fluids.** H. M. Rubinstein and J. D. Pryce (Postgrad. Med. School, London, England). *J. Clin. Path.*, 1959, **12**, 80–84.—A colorimetric ninhydrin method for amino-acid determination, based on that of Troll and Cannan (*J. Biol. Chem.*, 1953, **200**, 803), is described. EDTA (disodium salt) is used instead of pyridine to enhance colour development, thereby improving reproducibility by eliminating trace-metal interferences. Blanks are also lower than when pyridine is used. A separate buffer is used to maintain the pH optimum at 5·1. The method is applicable to simple soln. of amino acids, plasma, c.s.f., and urine. Results obtained on these biological fluids from normal subjects agree well with data reported for other methods in the past.

CHEM. ABSTR.

3428. **A new two-dimensional paper-chromatographic method applied to the separation of amino acids.** C. S. Knight (Res. Lab., W. & R. Balston Ltd., Springfield Mill, Sandling Road, Maidstone, Kent, England). *Nature*, 1959, **184** (Suppl. No. 19), 1486–1487.—Separation in one direction is achieved by making use of the ion-exchange properties of modified cellulose paper, and in the second direction a purely partition separation takes place (*cf. Anal. Abstr.*, 1959, **6**, 4214). For example, on cellulose phosphate paper, the solvents used are 0·02 *M* Na acetate buffer (pH 4·7) in one direction and *m*-cresol - aq. NH_3 in the other; the amino acids are anionic in the latter solvent and separate as on unmodified cellulose. On diethylaminoethylcellulose paper, the solvents are a buffer of pH 7·5 and *m*-cresol - aq. NH_3, respectively; the partition solvent inhibits ionisation of the exchange groups of the paper.

A. R. ROGERS

3429. **Two-dimensional system for the separation of amino acids and peptides on paper.** V. Richmond and B. S. Hartley (Dept. Biochem., Univ. Washington, Seattle, U.S.A.). *Nature*, 1959, **184** (Suppl. No. 24), 1869–1870.—Acid-free hydrolysates of 0·02 to 0·20 μmole of peptide are applied as 1-cm bands to Whatman No. 3 filter-paper. An amino-acid marker is run in parallel and the electrophoretic separation is carried out at pH 2·2 (4% v/v formic acid - 0·3% pyridine) at 2000 V for 70 min. At this pH the following groups of amino acids are separated—serine, glycine and aspartic acid, methionine, valine and tryptophan, and glutamic acid, threonine and alanine. Lysine is also well separated. The dry sheet is chromatographed at right angles to the direction of electrophoresis, with *n*-butanol - *n*-butyl acetate - acetic acid - H_2O (19:1:5:25) by the descending technique. Instead of chromatography in the second direction, high-voltage electrophoresis may be used. If carried out at pH 6·5, the basic amino acids are separated. The position of the spots is detected with dilute ninhydrin. The amino acids may subsequently be determined quantitatively.

S. BAAR

3430. **Application of Sakaguchi reaction to the quantitative estimation of arginine: a method involving paper chromatography.** K. R. Bhattacharya, J. Datta and D. K. Roy (Inst. Biochem. Expt. Med., Calcutta, India). *Arch. Biochem. Biophys.*, 1959, **84** (2), 377–392.—A study is made of the interference of other amino acids in the colorimetric determination of arginine, and the mechanism of the reaction in relation to the interference is discussed. Seven paper-chromatographic solvents for the preliminary separation of arginine are given, and the reaction is adapted for use on the chromatogram, from which the arginine spot is eluted with 1% $NaHCO_3$ for colorimetry. Results on some purified proteins are given.

W. H. C. SHAW

3431. **Improvements in methods for measuring hydroxyproline [in urine].** C. Mitoma, T. E. Smith, J. D. Davidson, S. Udenfriend, F. M. DaCosta and A. Sjoerdsma (Nat. Heart Inst., Bethesda, Md., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (6), 970–976.—Improved specificity in the method of Newman and Logan (*J. Biol. Chem.*, 1950, **184**, 299) is attained by extracting with diethyl ether the pyrrole-2-carboxylic acid derived from hydroxyproline by treatment with $CuSO_4$ and H_2O_2 followed by acidification. A modification in the concentration of acid and heat-development of the colour in the method described by Wiss (*Brit. Abstr. C*, 1949, 229) gives improved colour stability. Results obtained on urine samples from patients with various clinical conditions are given and discussed.

W. H. C. SHAW

3432. **Rapid and specific determination of threonine.** M. Flavin and C. Slaughter (National Heart Inst., Dept. Health, Educ. and Welfare, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1983–1984.—The acetaldehyde liberated by the periodate oxidation of threonine is measured colorimetrically with dihydrodiphosphopyridine nucleotide and alcohol dehydrogenase, the excess of periodate being first reduced with a thiol. The decrease in extinction at 340 mμ after adding the reagents is measured directly in the cell. The recovery of added threonine to protein hydrolysates was 98 to 107%.

G. P. COOK

3433. **Determination of ε-aminohexoic acid in urine by means of high-voltage paper electrophoresis.** A. Sjoerdsma and A. Hanson (Med. Clinic and Dept. of Clin. Chem., General Hospital, Malmö, Sweden). *Acta Chem. Scand.*, 1959, **13** (10), 2150–2151 (in English).—*Procedure*—A vol. of urine equiv. to 1 minute's excretion is diluted to 10 ml and 0·005 to

0·04-ml aliquots and reference standards of 5 to 40 μg of ε-aminohexoic acid (**I**) are applied to the paper 8 cm from the anode end and subjected to electrophoresis in formic acid - acetic acid - acetone - water (3:2:3:13, v/v) buffer (pH 1·2), for 1 hr. with a potential gradient of 50 V per cm and a current of 60 mA. The paper is dried at 80° for 1 hr., then sprayed with ninhydrin soln. [0·5% in *n*-butanol saturated with pyridine - acetic acid - water (10:1:95)] (pH 6), and the resulting purple colour is converted to the more stable light-red colour due to the copper complex by spraying with saturated $Cu(NO_3)_2$ soln. - 10% HNO_3 - water - methanol (1:0·2:4:95). The coloured spots are extracted with methanol and the extinction of the extract is measured at 508 mμ, with extracts from clear portions of the paper as a blank. Interference by alanine in the presence of large amounts of **I** is insignificant, but alanine can be separated by paper chromatography in the second dimension in a quick-running solvent of methanol - water - pyridine (20:5:1). E. J. H. Birch

3434. **Assay of L-phenylalanine in casein hydrolysates.** K. R. L. Mansford, A. Jones and S. M. Burns (Beecham Res. Lab. Ltd., Brockham Park, Surrey, England). *Analyst*, 1959, **84**, 750–751.—Four methods were examined—(*i*) a decarboxylase method, (*ii*) nitration by the Kapeller - Adlar - Kuhn method, followed by hydroxamic acid formation, (*iii*) a microbiological plate assay, and (*iv*) a microbiological tube-dilution assay. The results of the application of these methods are quoted. In the biological methods D-phenylalanine did not interfere until the ratio of D- to L-isomer exceeded 4:1, whereas both isomers were determined by the nitration method. Method (*i*), although simple, rapid and sensitive, involves a frequent time-consuming preparation of an acetone-dried powder of *Streptococcus faecalis*. In comparison, method (*ii*) is insensitive although it is reliable for normal casein hydrolysates. Method (*iv*) is expensive and laborious. Method (*iii*) with a mutant of *Escherichia coli* and the modified medium (Dickinson, *Ibid.*, 1958, **83**, 647; Jones and Burns, *Ibid.*, 1958, **83**, 648) is rapid, simple and reliable for casein hydrolysates, including those of the special caseins low in phenylalanine now used for phenylketonuria.
A. O. Jones

3435. **Method for the extraction and chromatographic separation of plasma iodoamino acids.** J. Wynn, I. Fabrikant and W. P. Deiss (Veterans Admin. Hosp., Durham, N.C., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **84** (1), 106–115.—Separation is carried out at 45° to 55° on columns of prepared Dowex 1-X2 ion-exchange resin eluted in gradient manner with 5 to 88% aq. formic acid. Mono- and di-iodotyrosine, 3:5-di-iodothyronine, 3:5:3′-tri-iodothyronine and thyroxine are separated from each other and from inorganic iodine. The method is applied to plasma (20 ml) obtained after the administration of $Na^{131}I$, and permits, after the addition of suitable carriers, the determination of an individual iodoamino acid having as few as 5 to 10 counts of ^{131}I per ml of plasma. W. H. C. Shaw

3436. **Peptide separation by two-dimensional chromatography and electrophoresis.** A. M. Katz, W. J. Dreyer and C. B. Anfinsen (Nat. Heart Inst., Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1959, **234** (11), 2897–2900.—A rapid separation of the peptides in proteolytic digests is effected by the use of descending chromatography with *n*-butanol - acetic acid - water (4:1:5), followed by electrophoresis with pyridine - acetic acid buffer at pH 3·7. Large sheets of Whatman No. 3 paper (18·25 in. × 22·5 in.) are used and this allows up to 80 peptide spots to be identified. After being dried the papers are treated with any one of a variety of reagents for identification of peptides or amino acids. The amount of protein hydrolysate used on a single paper is enough for a qual. amino-acid analysis, and the peptides from several papers can be pooled for quant. analysis. J. N. Ashley

3437. **Continuous electrophoresis [of serum proteins].** D. R. Davis and R. E. Budd (National Naval Med. Center, Bethesda, Md., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (6), 958–965.—The quantitative separation of serum proteins by electrophoresis in a commercial continuous-flow apparatus is described, and the precautions necessary to obtain satisfactory results are discussed.
W. H. C. Shaw

3438. **Important defects of paper electrophoresis [of proteins] and possibilities of overcoming them.** J. Pieper (Physiol.-Chem. Inst., Univ. Münster i. W.). *Z. ges. exp. Med.*, 1959, **131**, 359–371.—An elution method of determining proteins separated electrophoretically was found to be preferable to direct measurement. All the papers studied adsorbed protein, especially albumin, but a new material, "membrane foil", adsorbed almost none. The use of this material is advocated.
Nutr. Abstr. Rev.

3439. **Quantitative determination of protein fractions after electrophoresis in starch gel.** E. Habermann and B. Szopa (Pharmakol. Inst., Univ. Würzburg). *Z. ges. exp. Med.*, 1959, **131**, 520–524.—In the first procedure the stained electropherogram is immersed in a hot mixture of acetic acid - glycerol - water (1:10:200) to render it transparent, then fixed to a glass plate with agar and subjected to direct photometry. In the second procedure the required section of the stained gel is dried in acetone and dissolved in hot formic acid. Sodium hydroxide is added and the extinction of the soln. is measured at 630 mμ. Nutr. Abstr. Rev.

3440. **Estimation of protein in the cerebrospinal fluid, using the M.R.C. photometer.** J. G. Alexander and J. Parkes (Western Gen. Hosp., Hull, England). *J. Clin. Path.*, 1959, **12**, 91.—The proportion of c.s.f. to 3% aq. sulphosalicylic acid should be 1:4, not 1:3 as originally stated by Yeoman (*Ibid.*, 1955, **8**, 252). It was also found that the true protein level (x) was slightly higher than that obtained from the reading on the photometer (y), the two being related by the equation $x = (16y + 20)/15$. When the protein concn. exceeds 120 mg per 100 ml, it is necessary to dilute the c.s.f. with H_2O because the curve is no longer linear above this value. Use of saline as a diluent gives higher readings. Chem. Abstr.

3441. **Distribution of proteins in electrophoresis on a column of cellulose acetate by the method of Tiselius, Flodin and Porath.** J. Enselme, J. Tigaud and J. Frey (Fac. de Méd. et Pharm., Lyon, France). *Bull. Soc. Chim. Biol.*, 1959, **41** (11), 1373–1383.—The electrophoresis of serum proteins was carried out on a column of acetylated cellulose suspended in a barbitone buffer (pH 8·6, ionic strength 0·025)

and the distribution of individual proteins was compared with that obtained in free electrophoresis. The agreement is good, but some overlapping occurs and migration is more diffuse when cellulose acetate is present. Details are given of the preparation of the cellulose acetate, the apparatus employed and the methods of identification for individual proteins. S. M. MARSH

3442. **Optical rotatory dispersion of crystallised enzyme proteins.** B. Jirgensons (Texas Univ. Dept. Biochem., Houston, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **85** (2), 532–539.—A spectropolarimetric study is made of 16 crystalline enzymes, and their dispersion constants are tabulated. The significance of the observed values is discussed. W. H. C. SHAW

3443. **Spectrophotometric determination of elastin.** V. Scarselli (Univ. Milan, Italy). *Giorn. Biochim.*, 1958, **7**, 20–27.—Take 0·5 g of tissue or organ, mince it to 1-mm particles, wash with H_2O to free from blood, and filter. Extract this homogenate twice with acetone at room temp. for 7 hr., then once with diethyl ether for 12 hr., and dry at 70° for 14 hr. Triturate the dry matter, then macerate 40 to 50 mg in 10 ml of 0·1 *N* NaOH at 25° for 8 hr., centrifuge for 20 min., decant, wash the residue with 10 ml of ethanol at 38° for 20 min., centrifuge for 10 min. and decant. Add ethanolic orcein soln. [1 g of orcein in 100 ml of abs. ethanol; add 1 ml of HCl (*d* 1·19); dilute 1:10 with ethanol for use], 10 ml per 2·5 mg of supposed elastin, leave at 25° for 24 hr. (occasional stirring), centrifuge for 20 min., decant, wash several times with 10 ml of ethanol at 25° to complete (labile) colour removal, and evaporate off traces of ethanol at 38°. Add 5 ml of carbonate buffer (pH 10; equal vol. of 0·005 *M* soln. of carbonate and bicarbonate), leave at 38° for 3 hr., digest with 5 ml of 4% pancreatin soln. at 38° for 45 min. (occasional stirring), then centrifuge for 15 min. and leave for 1 hr. at room temp. Read the extinction at 590 mμ against a blank prepared with 5 ml of buffer and 5 ml of pancreatin soln. and calculate by reference to a standard curve. With elastin concn. of 5 mg per 100 g of dry organ, the method has a standard deviation of 1%. The sensitivity of the method is 0·067 mg of elastin. By this method the following elastin contents were determined (percentage of dry tissue or organ); ox tendon 0·28, rat brain 0·30, rat liver 0·44, rat muscle 1·35, rat heart 2·52, rat spleen 3·22, ox lung 3·36, rat lung 5·19, cat lung 5·25, and human aorta 45·32. CHEM. ABSTR.

3444. **Some improvements in colorimetric determination of elastin.** V. Scarselli (Ist. Biochim. Italiano, Via Brembo 65, Milano). *Nature*, 1959, **184** (Suppl. No. 20), 1563.—Modifications are made in the method described previously (*Anal. Abstr.*, 1960, **7**, 3443). A. R. ROGERS

3445. **Determination of [acetyl]neuraminic acid in crude brain lipids.** C. Long and D. A. Staples (Biochem. Div., Physiol. Dept., Inst. of Basic Med. Sci., Roy Coll. of Surg. of England, Lincoln's Inn Fields, London). *Biochem. J.*, 1959, **73** (3), 385–389.—The acid is determined spectrophotometrically by measurement of the "difference" extinction at 570 mμ of the products obtained after treatment with Bial's orcinol reagent. The reaction is carried out, on the untreated and acid-treated neuraminic acid, essentially according to Böhm *et al.* (*Anal. Abstr.*, 1954, **1**, 2755). This gives a reliable method for the determination of strandin, of which the most characteristic component is neuraminic acid. By using the same principle, the acid can also be determined with the EEL photo-electric colorimeter, with filter No. 626. J. N. ASHLEY

3446. **Determination of the reduced and oxidised pyridine nucleotides in animal tissues.** J. A. Bassham, L. M. Birt, R. Hems and U. E. Loening (M.R.C. Unit for Res. in Cell Metabol., Dept. of Biochem., Univ. of Oxford, England). *Biochem. J.*, 1959, **73** (3), 491–499.—Acid and alkaline extractions of the tissue are used to remove the oxidised and reduced forms, respectively, of the coenzymes. The four types are separated by treatment with specific enzymes (alcohol dehydrogenase and glucose 6-phosphate dehydrogenase) and selective destruction of oxidised and reduced forms with acid and alkali. The separated coenzymes are then determined fluorimetrically after being heated with 6 *N* NaOH to develop the fluorescence. The method is useful when the concn. of the coenzymes are as low as 1·5 μ*M* or when the amounts are as small as 10^{-10} mole. The advantages of the method, the conditions that affect the accuracy, and the specificity of the method are discussed. J. N. ASHLEY

3447. **Paper chromatography of sterols.** G. de Zotti, P. Capella and G. Jacini (Staz. Sper. Olii e Grassi, Milan). *Fette, Seif., Anstrichmitt.*, 1959, **61** (11), 1114–1119.—Sterols, their functional derivatives (*i.e.*, acetyl, benzoyl, aminoacetyl, chloroacetyl and malonyl) and keto derivatives can be separated by means of reversed-phase partition chromatography. Numerous solvent systems have been examined and the partition coefficients and R_F values are recorded. From these results systems suitable for the separation of the various types of compounds can be selected. Suitable developing agents are also described. The ratio of the cross-sectional areas occupied by the mobile and the stationary phases (*i.e.*, Am/As in Martin's equation) was determined for each solvent system. The methods (which are described in great detail) have been used for the separation of sterols in some vegetable oils. A. G. PETO

3448. **Micro-method for the simultaneous determination of cholesterol and iron in whole blood.** M. Mancini (Ist. Patolog. Spec. Med. e Metodol. Clin., Univ. Napoli, Italy). *Biochim. Appl.*, 1959, **6** (6), 404–407.—A procedure is described for the determination of cholesterol by the method of Anderson and Keys (*Clin. Chem.*, 1956, **2**, 145) and of Fe by reaction with 1:10-phenanthroline, with the same sample of whole blood. The method is also applicable to samples of blood stored by drying on filter-paper. The sample (0·1 ml) is hydrolysed by treatment with ethanolic KOH soln. (3 ml) for 5 hr. at 70°. Cholesterol is extracted with light petroleum and Fe is determined in the aq. phase after destruction of organic matter by treatment with HNO_3 (2 ml), H_2SO_4 (0·5 ml) and finally with $HClO_4$ (0·5 ml). E. C. APLING

3449. **Modified method for a more precise and simple determination of serum cholesterol.** B. D'Alessandro, A. Brancaccio and S. Pedicini (Ist. Semeiotica Med., Univ. Napoli, Italy). *Biochim. Appl.*, 1959, **6** (6), 331–337.—The method described is a modification of those of Kanter *et al.* (*J. Lab. Clin. Med.*, 1952, **40**, 303) and Kingsley and

Schaffert (*J. Biol. Chem.*, 1949, **180**, 315). *Procedure for total cholesterol*—Mix serum (0·3 ml) and $CHCl_3$ (9·7 ml) in a stoppered centrifuge tube and shake for 5 min. Add $MgSO_4$ (1·5 g) and shake again for 5 min. Add fuller's earth (0·5 g) and centrifuge. Shake an aliquot of the soln. (5 ml) with 2 ml of acetic anhydride - H_2SO_4 (9:1), set aside for 15 min., and read the extinction at 540 mμ. *Procedure for esterified cholesterol*—Treat a second aliquot of serum in a similar manner, but with a 0·1% soln. of digitonin in $CHCl_3$ for the extraction, and adding glacial acetic acid (0·2 ml) after the addition of $MgSO_4$. A water blank and a standard soln. of cholesterol are treated similarly at the same time. The method is speedy and precise. Recoveries of added cholesterol ranged from 89 to 94%.

E. C. APLING

3450. **Determination of urinary pregnanediol.** M. F. Jayle, O. Judas and O. Crépy (Lab. de Chim. Biol., Fac. de Méd., 45 rue Saints-Pères, Paris, France). *Bull. Soc. Chim. Biol.*, 1959, **41** (11), 1441–1454.—The methods of Klopper *et al.* (*J. Endocrinol.*, 1955, **12**, 209), Gutermann and Schroeder (*J. Lab. Clin. Med.*, 1948, **33**, 356) modified by Piaux *et al.* (*Gynéc. et Obstét.*, 1953, **52**, 441), Huber (*Biochem. J.*, 1947, **41**, 609) modified by Watteville *et al.* (*J. Clin. Endocrin.*, 1948, **8**, 982) and Crépy *et al.* (*Bull. Soc. Chim. Biol.*, 1956, **38**, 506) are critically compared. Two simplifications of the Klopper method are presented and the results are compared with those by the original procedure. The sensitivity and accuracy of one of these are as satisfactory as those of the original method. *Procedure*—The urine is extracted with *n*-butanol at pH 8 to 9 and the extract is washed, evaporated *in vacuo* and dissolved in acetate buffer (pH 5·2). β-Glucuronidase (1000 units per ml) is added and hydrolysis is continued at 37° for 12 to 18 hr. The hydrolysate is extracted with diethyl ether - ethanol (4:1) and the extracted material is dissolved in benzene and chromatographed on alumina. The material eluted with benzene containing 3% ethanol is dissolved in conc. H_2SO_4 and the extinction is measured at 390, 430 and 470 mμ after 1 hr. at 25°. The results are corrected by the method of Allen and referred to a calibration curve. If the butanol extraction is omitted, the method is less specific and precise, but is still sufficiently accurate for routine clinical measurements.

S. M. MARSH

3451. **Development of a specific method of determination for pregnanediol, pregnanetriol and 20-oxopregnanediol [in urine].** R. Henry and M. Thevenet (Centre d'Étud. Biol., l'Hôp. Tenon, Paris, France). *Bull. Soc. Chim. Biol.*, 1959, **41** (11), 1391–1425.—A series of preliminary experiments on the hydrolysis, separation and determination of pregnanediol (**I**), pregnanetriol (**II**) and 20-oxopregnanediol (**III**), designed to develop specific methods of determination, is fully described. The suggested procedure is as follows. The sample is hydrolysed at pH 5·2 and 37° for 18 hr. with 1000 units of glucuronidase per ml. The mixture is extracted with benzene or trichloroethylene (3 × 35 ml) and the extracts are washed, filtered and distilled *in vacuo*. The residue is dissolved in benzene and chromatographed on a column of activated alumina, and the steroids are separated by eluting with benzene containing various amounts of methanol (0·5% for **I**, 1% for **III** and 2·5% for **II**). The eluates are evaporated to a sticky consistency, dissolved in 20% H_2SO_4 and the extinctions of the soln. are measured against the acid. Soln. of **I** are measured at 380, 350 and 320 mμ after being set aside for 30 min. at 25° in the dark; a correction formula is applied, and the results are referred to a calibration curve. A similar procedure is used for soln. of **II** at 470, 440 and 410 mμ after 2 hr. at 25° and for soln. of **III** in conc. H_2SO_4 between 280 and 450 mμ after 2 hr. at 25°; **III** may also be determined photometrically at 380 mμ as the dinitrophenylhydrazine derivative. The method is sensitive and reproducible and can be applied to the determination of ≃ 100 μg of **I**, 50 μg of **II** and 500 μg of **III**.

S. M. MARSH

3452. **Analytical study of steroids of the pregnanetriol group.** S. Weinmann, J. Weinmann, E. E. Baulieu, P. Desgrez and M. F. Jayle (Lab. de Chim. Biol., Fac. de Méd., 45 rue Saints-Pères, Paris, France). *Bull. Soc. Chim. Biol.*, 1959, **41** (11), 1427–1440.—Pregnanetriol steroids which are not oxygenated in the C_{11} position can be separated by paper partition chromatography in the system *cyclo*hexane - benzene (1:1) - propane-1:2-diol - methanol (1:1) at 25°. Pregnanetriols oxygenated at C_{11} can be separated by using a volatile stationary phase of toluene - ethyl acetate - methanol - water (9:1:5:5) at 35°. Results are tabulated for typical mixtures, together with R_F values and colour reactions of the individual steroids. The visible absorption spectra of the pregnanetriols in conc. H_2SO_4 soln. have been studied. Pregn-5-enetriol shows marked differences and can be determined in the presence of other pregnenetriol isomers by (*i*) measuring the extinction at 510 mμ and applying an equation, or (*ii*) measuring the extinctions at 408 and 436 mμ and comparing with a calibration curve. The accuracy of both methods is ≃ 5%. The infra-red spectrum of pregn-5-ene-3β,17α,20β-triol in the region 7 to 15 μ is described. The significance of the results in relation to the determination of the metabolites of 17α-hydroxyprogesterone and 21-deoxycortisol is discussed.

S. M. MARSH

3453. **The effectiveness of various types of hydrolysis in the extraction and determination of steroids with 21 carbon atoms.** A. Brancaccio, B. D'Alessandro and G. Jacono (Ist. Semeiot. Med., Univ. Napoli, Italy). *Biochim. Appl.*, 1959, **6** (6), 367–370.—After a study of extraction with butanol, acid hydrolysis in the cold and in the warm, and enzymic hydrolysis with β-glucuronidase, the method recommended involves enzymic hydrolysis with both β-glucuronidase and sulphatase (added as the digestive juice of *Helix pomatia*), and extraction with dichloromethane.

E. C. APLING

3454. **Chromatographic separation of some Δ^4-3-oxosteroids.** Tokuichiro Seki (Dept. of Genetics, Osaka Univ. Med. Sch., Japan). *J. Chromatography*, 1959, **2** (6), 667–669 (in English).—The separation of some Δ^4-3-oxosteroids on a partially esterified cation exchanger [Amberlite IRC-50, boiled with a mixture of ethanol, methanol and 2 *N* HCl (15:5:6) for 40 hr.] is described. The steroids are applied to the column as a soln. in ethanol - methanol - H_2O (15:5:11) and eluted with the same solvent, and the extinction of each eluate fraction is measured at 240 mμ.

G. S. ROBERTS

3455. **Determination of 17-oxosteroids, dehydro-*epi*androsterone and androsterone in plasma and urine.** B. D'Alessandro, A. Brancaccio and G. Jacono (Ist. Semeiot. Med., Univ. Napoli, Italy).

Biochim. Appl., 1959, **6** (6), 338–349.—The importance for diagnostic purposes of the simultaneous determination of steroids in peripheral blood and in urine by identical methods is emphasised and a suitable procedure is described. *Procedure*—For plasma (30 ml), precipitate the protein with ethanol (150 ml), and wash with ethanol (60 ml); evaporate the soln. at 40° in a stream of N, and dissolve the residue in water (30 ml). Hydrolyse the plasma extract or whole urine (50 ml) by incubation for 48 hr. at 37° and pH 5 (acetate buffer) with the digestive juice of *Helix pomatia* (containing 100,000 units of β-glucuronidase and 50,000 units of sulphatase activity per ml) (0·3 ml for plasma samples, or 0·5 ml for urine), and then shake with diethyl ether (120 ml) for 48 hr., after adjusting the pH to 0·8 with H_2SO_4. Wash the ether soln. twice with a 10% soln. of $NaHCO_3$ and twice with H_2O, and evaporate to dryness. [Then dissolve the plasma extracts in 70% ethanol (20 ml), wash with hexane (3 × 15 ml), add H_2O (10 ml), extract with $CHCl_3$ (3 × 15 ml), and evaporate to dryness.] Dissolve the residue in ether (20 ml) and pass the soln. through a column (70 mm × 10 mm) of activated Florisil. Elute with ether containing 2·5% of methanol (35 ml), wash the eluate twice with *N* NaOH and twice with H_2O and divide into three portions for the determination of (*i*) total 17-oxosteroids, (*ii*) ketonic steroids only, and (*iii*) dehydro-*epi*androsterone (**I**) and androsterone (**II**). For (*i*), evaporate to dryness and dissolve the residue in ethanol (0·2 ml), add a 1% soln. of *m*-dinitrobenzene in ethanol (0·2 ml) and 2·5 *N* ethanolic KOH (0·2 ml), incubate in the dark for 90 min. at 25°, add ethanol (5 ml) and measure the extinction at 460, 520 and 580 mμ. For (*ii*), develop the colour as described for (*i*), but add H_2O (0·6 ml) and $CHCl_3$ (0·6 ml), shake gently, centrifuge, reject the $CHCl_3$ layer and read the extinctions at the same wavelengths. For (*iii*), develop a paper chromatogram with kerosine - methanol - water (5:4:1), elute areas corresponding to **I** and **II**, and develop the colours as described for (*ii*). Interpret the extinctions by application of Allen's formula, and comparison with values obtained by treating known amounts of **I**. Recoveries of **I** plus **II** were from 94 to 98%. E. C. Apling

3456. **Paper chromatography of corticosteroids at room temperature.** J. Tuzson (State Inst. Public Health, Univ. Med. School, Budapest). *Nature*, 1959, **184** (Suppl. No. 25), 1937.—Steroids (1 to 200 μg) dissolved in methanol are applied to S. & S. 2043/*b* paper. The paper, with the exception of the starting line, is then impregnated with 90% methanol, the excess of methanol being removed by blotting. The chromatography chambers contain filter-paper wads saturated with 90% methanol and the organic phase of the solvent. Several solvent systems were tested, including toluene - ethanol - light petroleum - H_2O (2:6:1:3) and toluene - methanol - H_2O (10:7:3). All were used at room temperature. The spots are detected with an alkaline soln. of blue tetrazolium or 15% H_3PO_4. S. Baar

3457. **Present views on the determination of corticosteroids in plasma and urine. A proposed unified method.** A. Brancaccio, B. D'Alessandro and G. Jacono (Ist. Semeiot. Med., Univ. Napoli, Italy). *Biochim. Appl.*, 1959, **6** (6), 377–387.—Available methods are critically reviewed and a detailed procedure is described. The method involves ethanolic extraction of plasma, partition of the plasma extract, or urine, between H_2O and a mixture of light petroleum and $CHCl_3$, and extraction of the free corticosteroids with dichloromethane. The combined corticosteroids are then liberated by enzymic hydrolysis with β-glucuronidase and sulphatase and extracted separately with dichloromethane. The separate extracts (in $CHCl_3$) are finally purified by passage through a Florisil column and elution with a 25% soln. of methanol in $CHCl_3$. Aliquots of the eluate are examined colorimetrically by reaction with (*i*) blue tetrazolium, (*ii*) phenylhydrazine, and (*iii*) isoniazid. Reaction (*i*) measures total corticosteroids, (*ii*) measures cortisol and its derivatives, and (*iii*) measures only the "biologically active" fraction. Recoveries of added cortisol were ≃ 95%. E. C. Apling

3458. **Studies on sulphatases. XXV. Determination of $Ba^{16}SO_3{}^{18}O$ by infra-red spectroscopy.** B. Spencer (Dept. of Biochem., Univ. of Wales, Cardiff). *Biochem. J.*, 1959, **73** (3), 442–447.—The method is based on measurement of the relative extinctions of $BaSO_4$ at 981 cm^{-1} and 961 cm^{-1}. It is used for the determination of $BaS^{16}O_3{}^{18}O$ in $BaSO_4$, and is insensitive compared with the mass-spectrographic method; it is of little use with samples that contain low concn. of ^{18}O or when small differences in isotope content are to be measured. But when applicable it has the advantages of speed and simplicity. J. N. Ashley

3459. **Modified spectrophotometric determination of chymotrypsin, trypsin and thrombin.** B. C. W. Hummel (Food and Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Ont., Canada). *Canad. J. Biochem. Physiol.*, 1959, **37** (12), 1393–1399.—The Schwert and Takenaka method (*Anal. Abstr.*, 1955, **2**, 2838) is modified in some manipulative details and by using as substrates toluene-*p*-sulphonyl-L-arginine methyl ester (**I**) in place of α-benzoyl-L-arginine ethyl ester (**I** is not hydrolysed by chymotrypsin) and benzoyl-L-tyrosine ethyl ester (**II**) in place of N-acetyl-L-tyrosine ethyl ester. Both these substrates give enhanced sensitivity. Measurements are made at 30° ± 0·1° of the difference between the extinctions of the ester and free acid in a u.v. spectrophotometer, with substrate and buffer in both cells and the enzyme in one cell so that a direct reading of the difference is obtained. Measurements are made every 30 sec. to determine the rate of hydrolysis. The rate of hydrolysis of **II** by chymotrypsin is 3·8 × 10^{-3} extinction units at 256 mμ (≡ 0·14 μmole) per min. per μg of enzyme per ml, that of **I** by trypsin is 101 × 10^{-3} units at 247 mμ (≡ 0·86 μmole), and by thrombin, 0·44 × 10^{-3} units (≡ 0·0038 μmole). The initial rate of hydrolysis is proportional to the enzyme concn. in the range 0·5 to 3·0 μg per ml for chymotrypsin, 0 to 0·15 μg per ml for trypsin and 0 to ≃ 20 μg per ml for thrombin. E. J. H. Birch

3460. **Creatine and creatine kinase measurement.** M. L. Tanzer and C. Gilvarg (Dept. of Biochem., New York Univ. Coll. of Med., U.S.A.). *J. Biol. Chem.*, 1959, **234** (12), 3201–3204.—An enzymic method is described. Creatine kinase is combined with pyruvate kinase and lactic dehydrogenase, whereby the conversion of creatine into its phosphate is accompanied by the oxidation of an equimolar amount of reduced diphosphopyridine nucleotide; the change in extinction at 340 mμ is then a direct measure of the amount of creatine in

the soln. Creatinine, arginine, citrulline, ureidosuccinate, canavanine and glycocyamidine have no effect on the assay. Only glycocyamine interferes; if its amount is equal to that of the creatine there is a 2% error. Creatine kinase activity is measured with the same enzyme system pre-saturated with creatine. J. N. ASHLEY

See also Abstracts—**3105**, Automation for determination of amino acids. **3144**, Mg in tissues. **3216**, Sulphates in biological material. **3317**, Separation of aldonic acids. **3479**, Assay of vasopressin and oxytocin. **3480**, Assay of anti-haemophilic globulin. **3485**, Azacyclonol in urine. **3497**, Betaine in sugar juices. **3498**, Amino acids in sugar juices. **3499**, Glutamine in sugar juices. **3511**, Mannan in coffee. **3525**, Tocopherols in tissues. **3546**, Gas regulation in metabolic studies.

Pharmaceutical analysis

3461. **Gas chromatography in routine pharmaceutical analysis.** C. B. Baines and K. A. Proctor (Physical Assay Div., Standards Dept., Boots Pure Drug Co. Ltd., Nottingham, England). *J. Pharm. Pharmacol.*, 1959, **11** (Suppl.), 230T–234T.—To determine camphor, menthol or volatile oils in pharmaceutical preparations, use 20% of squalane on Celite (100 to 120 mesh) at 130° as stationary phase, with a mixture of H and N (4:1) as carrier gas at a flow-rate of 100 ml per min.; ethylbenzene is a suitable internal standard. To determine diethyl phthalate, use 30% of Na dodecylbenzenesulphonate (Arylan S.90) on Chromosorb (36 to 85 mesh) at 225° as stationary phase, with a mixture of H and N (4:1) as carrier gas at a flow-rate of 60 ml per min.; 1-phenylpropanol is a suitable internal standard. A. R. ROGERS

3462. **Microchemical identification of some alkaloids, barbiturates, sulphonamides and other synthetic drugs. IV.** T. P. A. van der Wegen (Farm. Lab. Rijksuniv., Utrecht, Netherlands). *Pharm. Weekbl.*, 1959, **94** (23), 749–762.—Microchemical reactions are given for the following drugs—nicotine, nicotinic acid, homatropine methylbromide, procaine, proguanide, tetracaine, the hydrochlorides of dibucaine, benzylmorphine, methamphetamine and meperidine, allyl*cyclo*hexenylbarbituric acid and promethazine. (44 illustrations.)

V. T. P. A. van der Wegen. *Ibid.*, 1959, **94** (24), 781–796.—Microchemical reactions are described for physostigmine, neostigmine, *pseudo*cocaine, tropacocaine, trigonelline, (+)-tubocurarine, barbiturates and sulpha drugs. (54 illustrations.)
M. J. MAURICE

3463. **Spectrophotometric determination of certain alkaloids and application to pharmaceutical preparations.** A. H. J. Cross, D. McClaren and S. G. E. Stevens (Smith, Kline and French Laboratories, Ltd., Welwyn Garden City, Herts., England). *J. Pharm. Pharmacol.*, 1959, **11** (Suppl.), 103T–107T.—To determine atropine, hyoscyamine, quinine, quinidine, brucine, strychnine or physostigmine, add 1% Na picrate soln. (3 ml) to a soln. of the alkaloid (≃ 1 mg) in phosphate buffer soln. (pH 7·00 ± 0·05) (20 ml), extract with $CHCl_3$ (3 × 25 ml), shake the combined extracts with phosphate buffer soln. (pH 11·2 to 11·5) (40 ml), dilute the aq. phase with the same buffer soln. to 100 ml, and measure the extinction at 355 mμ. The method has been applied to injections, tablets and other pharmaceutical preparations. The results are in agreement with those obtained by the official methods.
A. R. ROGERS

3464. **Rapid and sensitive method of quantitative determination of apomorphine.** P. N. Kaul, E. Brochmann-Hanssen and E. L. Way (Univ. of California Sch. Pharm. and Dept. Pharmacol., Sch. Med., San Francisco). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (11), 638–641.—This colorimetric method is based on that of Grimbert and Leclere (*J. Pharm. Chim.*, 1915, **11**, 23), in which the product of oxidation of apomorphine (**I**) with $HgCl_2$ soln. is extracted with amyl alcohol. *Procedure*—Mix the sample soln. (4 ml containing 60 to 120 μg of **I**) with McIlvaine buffer of pH 6 (1 ml) and saturated aq. $HgCl_2$ soln. (3 drops), heat in a bath of water at 70° for 3 or 4 min., cool to room temp., shake for 1 min. with *iso*amyl acetate (10 ml), then centrifuge; measure the extinction of the upper layer at 330 mμ. To determine **I** in biological fluids, extract the diluted sample with *iso*amyl acetate at pH 6 to 7 and re-extract **I** into 0·05 *N* HCl before assay. Catechol, adrenaline, noradrenaline and dihydroxyphenylalanine do not interfere. A. R. ROGERS

3465. **Results obtained by the application of different techniques of determination of alkaloids contained in belladonna powder.** J. Delga, C. Pallaget and J. Cariou (Hôpital Militaire du Val-de-Grâce, France). *Ann. Pharm. Franç.*, 1959, **17** (7–8–9), 522–531.—The different results given by the methods of various pharmacopoeias (French 1937 and 1949, German, British, Belgian, International, Swiss and U.S.) for the analysis of belladonna powders are investigated. The determination of the different alkaloids in the extracts by electrophoresis or chromatography does not enable more than two groups to be characterised (atropine plus hyoscyamine and hyoscine). The differences between different methods of evaluating the same extract are accounted for by the fact that the results in all cases are expressed as atropine and that a mixture of alkaloids takes part in the reactions and that, in particular, the physiological activity is greater (1·6 to 1·8 times) for hyoscyamine than for atropine. The effect of heating the extract is investigated and attributed to racemisation of the hyoscyamine. Since the chemical assay is not proportional to the physiological effect it is recommended that a physiological method should be used (*cf. Ibid.*, 1959, **17**, 531). E. J. H. BIRCH

3466. **Colorimetric estimation of emetine in ipecacuanha.** J. P. S. Sarin, R. C. Nandi and G. K. Ray (Central Drug Res. Inst., Lucknow, India). *Indian J. Pharm.*, 1959, **21** (11), 308–309.—Mix a soln. of emetine (**I**) (5 to 20 μg) in acetate buffer soln. (pH 4·6) (2 ml) with a freshly prepared 0·04% soln. of methyl orange in buffer (2 ml), shake for 2 min. with $CHCl_3$ (10 ml) and set aside for 30 min. Separate the $CHCl_3$ layer and immediately measure the extinction at 420 mμ. To determine **I** in powdered ipecacuanha root or in tincture of ipecacuanha, follow the assay method of the International Pharmacopoeia 1955 as far as preparation of an acid extract but, instead of adding aq. NH_3 and extracting with $CHCl_3$, add NaOH soln. until the extract is alkaline, shake with diethyl ether, dissolve the extracted **I** in buffer soln. and treat an aliquot portion as described above.
A. R. ROGERS

3467. **Studies on the determination of alkaloids from *Rauwolfia serpentina*. VII. Fluorimetric determination of reserpine on filter-paper. (2).** Kazutaka Yamaguchi, Toshikazu Tabata and Hatsue Shōji (Nat. Hyg. Lab., Tamagawa-yogamachi, Setagayaku, Tokyo). *J. Pharm. Soc. Japan*, 1959, **79** (4), 476–478.—Various amounts of reserpine are spotted on to a Whatman No. 1 filter-paper and submitted to paper electrophoresis with 5 *N* acetic acid as electrolyte at 700 V for 2 hr. After migration, the separated spot was heated with the mixed vapours of H_2O_2 and acetic acid at 105°. A linear relationship was found between the amount of reserpine and the intensity of fluorescence. To obtain accurate results with rauwolfia extract, the reserpine fraction must be separated from strong bases by extraction with buffer soln. before electrophoresis. S. NATORI

3468. **Paper chromatography of clavine alkaloids.** D. Gröger (Arbeitsstelle für Biochemie der Pflanzen, Halle Dtsch. Akad. Wissenschaft., Berlin). *Arch. Pharm., Berlin*, 1959, **292** (11), 649–651.—The paper is impregnated with formamide - ethanol (2:3), and thoroughly dried, and the chromatogram is developed with dichloromethane satd. with formamide at 22° for 3 to 4 hr. Penniclavine, *iso*penniclavine, setoclavine and *iso*setoclavine are detected by their fluorescence in u.v. light. These alkaloids and agroclavine, chanoclavine and elymoclavine yield a blue coloration with a 3·3% soln. of *p*-dimethylaminobenzaldehyde in 25% HCl. A. G. COOPER

3469. **Studies on digitalis. IV. Products in the reaction of B-series glycosides in *Digitalis purpurea* L. with Jensen's reagent for fluorescence determination. (1). Studies by paper partition chromatography.** Toshiro Sasakawa (Takeda Pharm. Ind., Ltd., Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1959, **79** (5), 571–574.—The determination with Jensen's reagent (*Anal. Abstr.*, 1956, **3**, 2852) of digitalis glycosides that do not contain deoxy sugars [such as digitalinum verum (**I**) and strospeside (**II**)] gives values higher than the theoretical unless the reaction is allowed to proceed for several hours. To discover the cause, gitoxigenin (**III**), **II**, purpurea glycoside B (**IV**), **I** and gitorin (**V**) were allowed to react with Jensen's reagent and the products were examined by paper chromatography at regular intervals during the reaction. Glycosides such as **IV** and **V** that contain a deoxy sugar are hydrolysed to **III**, which is dehydrated to $\Delta^{14,16}$-dianhydrogitoxigenin (**VI**) and shows fluorescence; glycosides that do not contain a deoxy sugar form intermediates which are hydrolysed to give **VI**, the reaction proceeding more slowly than with **IV** and **V**.

V. Products in the reaction of B-series glycosides in *Digitalis purpurea* with Jensen's reagent for fluorescence determination. (2). Studies on the intermediates in the reaction of digitalinum verum or strospeside with Jensen's reagent for the determination of B-series glycosides in *Digitalis purpurea*. Toshiro Sasakawa. *Ibid.*, 1959, **79** (5), 575–578.—The intermediates in the reaction of **I** or **II** with Jensen's reagent were isolated and identified as their respective $\Delta^{14,16}$-dianhydro derivatives (**VII** and **VIII**). These exhibit stronger fluorescence than **VI**. The reason why the determination of **I** and **II** gave higher values than the theoretical for the first several hours is due to the formation of **VII** and **VIII**. Further treatment of **VII** and **VIII** with the reagent affords **VI** and it is necessary to effect the determination after several hours to complete the hydrolysis to **VI**. S. NATORI

3470. **Recommended methods of assay of crude drugs. Determination of rotenone in rotenone-bearing plants with special reference to lonchocarpus.** Pharmaceutical Society of Great Britain and the Society for Analytical Chemistry, Joint Committee on Methods of Assay of Crude Drugs. *Analyst*, 1959, **84**, 735–742.—The sample, when in the form of resin, is dissolved in a mixture of benzene and diethyl ether and the soln. is shaken with aq. KOH soln. according to a specified procedure, the alkaline layer being rejected. The benzene - ether layer is mixed with water, then just acidified with HCl, the aq. layer is removed and the organic layer is dried with Na_2SO_4. The solvent is removed by distillation under reduced pressure, the residue is dissolved by heating under reflux with CCl_4 saturated with rotenone, and the soln. is cooled with ice water until crystallisation is complete. The crystals, consisting of the equimolecular solvate, are collected and weighed, and the optical rotation of a 4% soln. in benzene is measured. A 4% soln. of the pure complex has an optical rotation of −166°. For the ground root the method is applied to the $CHCl_3$ extract of the sample. A. O. JONES

3471. **Outline of details for assaying the commonly used antibiotics.** A. Kirshbaum and B. Arret (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1959, **9** (10), 613–617.—Details of 36 bioassay methods for 17 antibiotics are tabulated in such a way as to permit an analyst familiar with bioassays to carry out the methods without further reference. W. H. C. SHAW

3472. **Errors caused by stainless-steel cylinders in plate bioassays.** N. S. Snell and J. C. Lewis (Western Regional Res. Lab., U.S. Dept. Agric., Albany, Calif., U.S.A.). *Antibiot. & Chemother.*, 1959, **9** (10), 609–612.—Loss of potency is found to occur in solutions of bacitracin, chlortetracycline, potassium penicillin G, aterrimin and subtilin in contact with the stainless-steel cylinders specified in certain F.D.A. methods. The loss varied with potency and was found to be greater with tarnished cylinders. W. H. C. SHAW

3473. **Consideration of factors affecting the iodimetric assay of penicillin.** P. J. Weiss (Food and Drug Admin., U.S. Dept. of Health, Education and Welfare, Washington, D.C.). *Antibiot. & Chemother.*, 1959, **9** (11), 660–666.—Interference by the degradation products of penicillin is detected by high blank values. The error is negligible if $> 75\%$ of the penicillin present is active, and is small if 25 to 75% is still active. Interference by streptomycin, dihydrostreptomycin, neomycin, novobiocin or sodium gentisate is eliminated or diminished by reducing the pH of the blank soln. to $< 2{\cdot}0$ immediately before titration. Nitrofurazone interferes and must be removed before the assay. The apparent recovery of penicillin from soln. containing $<$ 1600 units per ml is $> 100\%$, and for high accuracy a calibration curve should be used. A. R. ROGERS

3474. **Application of Analmatic batch-handling equipment to the determination of penicillin in fermentation broths.** N. C. Green and P. R. Monk (Glaxo Lab. Ltd., Ulverston, Lancs., England). *Chem. & Ind.*, 1959, (39), 1210–1214.—The method

of Pan (*Anal. Abstr.*, 1955, **2**, 448) for the determination of penicillin is operated on a semi-automatic basis, with automatic dispensing of reagents and transfer of solutions, and final determination with a recording absorptiometer. The over-all precision (95% confidence limits) is ± 2·5% (400 assays) and two assistants can perform 400 assays in a day. The operation of the automatic pipette systems is described. E. J. H. BIRCH

3475. **Determination of polymyxin activity by agar diffusion.** V. S. Dimitrieva and S. M. Semenov (All-Union Antibiotics Sci. Res. Inst.). *Antibiotiki*, 1959, **4** (6), 92–96.—Two methods are described. (*i*) With *Brucella bronchoseptica* as test organism, the curve of dose plotted against diameter of zone of inhibition is linear from 50 to 250 units per ml. (*ii*) With *Escherichia coli*, a preliminary diffusion of polymyxin soln. into the medium is carried out for 18 to 20 hr. at 4° to 6° in order to limit the growth of the organism. The dose - inhibition curve is linear from 100 to 800 units of polymyxin. K. R. C.

3476. **Chemical methods for the determination of antibiotics. VIII. Colorimetric determination of viomycin.** Kiichiro Kakemi, Takaichi Arita and Sada Ohashi (Pharm. Inst., Med. Fac., Kyoto Univ., Sakyo-ku). *J. Pharm. Soc. Japan*, 1959, **79** (4), 531–533.—An aq. soln. of viomycin sulphate (4 ml) is cooled to 0° to 5°, 20% KOH soln. (1 ml) and 0·1% 8-hydroxyquinoline soln. (0·3 ml) are added and, after shaking, NaBrO soln. (0·5 ml). The mixture is shaken for 1 min. and pyridine (2 ml) is added to stabilise the colour. The absorption maximum at 507 mμ is used for the determination, and the results are in good agreement with the potency determined by biological assay. S. NATORI

3477. **The characterisation of crystalline and amorphous aloin.** R. E. Lister and R. R. A. Pride (Res. Dept., J. F. Macfarlan & Co. Ltd., Edinburgh, Scotland). *J. Pharm. Pharmacol.*, 1959, **11** (Suppl.), 278T–282T.—Amorphous aloin differs from the crystalline aloin described in the B.P. 1953 in its microscopic appearance, its high solubility in water and its u.v. absorption spectrum. An aq. soln. of amorphous aloin is almost transparent at 354 mμ, whereas the extinction of an aq. soln. of crystalline aloin at 354 mμ is greater than that at 298 mμ. The amorphous material contains little barbaloin and is of low biological potency when assayed by the rat faecal consistency method. A. R. ROGERS

3478. **A sloping screen method for the bioassay of insulin in mice.** N. R. Stephenson (Lab. of the Food and Drug Directorate, Dept. of Nat. Health and Welfare, Ottawa, Canada). *J. Pharm. Pharmacol.*, 1959, **11** (11), 659–665.—A quantal response method for the bioassay of insulin (**I**) is described in which a sloping screen (*cf.* Thompson, *Endocrinology*, 1946, **39**, 62) is used for the detection of hypoglycaemic symptoms in mice treated with **I**. In a comparison of this method with that of the B.P. 1958, it was found that the former needed a larger dose of **I**, although the slopes of the log dose - response curves did not differ significantly. Addition of a retarding agent such as gelatin or protamine to the **I** does not influence the slope. Mice primed with 0·005 unit of **I** before their routine use in assays are more uniform in their response than unprimed mice. Prolonged exposure of the mice to daylight probably reduces the precision of the assay. A. R. ROGERS

3479. **Specific and sensitive assay method for vasopressin and oxytocin using glass[-fibre] paper chromatography.** A. Arimura and J. F. Dingman (Endocrine Unit, Dept. Med., Tulane Univ. Sch. Med., New Orleans, La., U.S.A.). *Nature*, 1959, **184** (Suppl. No. 24), 1874–1875.—The chromatography of vasopressin and oxytocin is carried out on glass-fibre paper (6 cm × 15 cm) impregnated with silicic acid (*cf.* Dieckert *et al.*, *Anal. Chem.*, 1958, **30**, 1442) and dried at 150° to 200°. About one milli-unit of vasopressin can be separated with *n*-butanol - ethanol - aq. NH_3 (6:3:1) as solvent and a similar concn. of oxytocin with *n*-pentanol - acetic acid (16:1) saturated with H_2O. The separations take 30 and 50 min., respectively. The peptides are detected by spraying the air-dried chromatogram with Folin's phenol reagent followed, after partial drying, with satd. Na_2CO_3 soln. As little as 0·5 μg of peptide can be detected. Five spots were separated from a commercial preparation of vasopressin; the spot at R_F 0·71 had the same R_F value as lysine vasopressin and when eluted possessed 93% of the total biological activity. Commercial oxytocin when separated in the appropriate solvent showed 2 to 3 spots, 99% of the total biological activity being in the spot of R_F 0·71. A suitable eluting agent contains 8 g of NaCl, 0·42 g of KCl, 0·06 g of $CaCl_2$, 1 g of $NaHCO_3$, 0·45 g of NaH_2PO_4 and 0·1 g of $MgCl_2$, per litre, and the eluates are assayed by biological techniques. S. BAAR

3480. **The assay of anti-haemophilic globulin.** R. M. Savage (S. Maw, Son and Sons Ltd., Aldersgate House, Barnet, Herts., England). *J. Pharm. Pharmacol.*, 1959, **11** (Suppl.), 149T–156T.—The method of Biggs *et al.* (*Brit. J. Haemat.*, 1955, **1**, 20) is examined and some modifications are discussed. The statistical design and analysis is offered in a simple form suitable for routine application. The method is satisfactory if certain precautions are taken and if the interpretation is carried out objectively by mathematical analysis. A. R. ROGERS

3481. **The analysis of phenobarbitone and acetylsalicylic acid mixtures using ion-exchange resins.** E. G. Clair and N. C. Nair (Pharm. Chem. Sect., Food and Drug Directorate, Dept. of National Health and Welfare, Ottawa, Canada). *Drug Standards*, 1959, **27** (6), 172–177.—Prepare the anion-exchange resin Dowex 3, in 60 to 80-mesh powder, by extracting with 95% ethanol in a Soxhlet apparatus for 24 hr., and washing with acetate buffer soln. in 50% ethanol (pH 4·6) until the washings are transparent at 240 mμ. Suspend the powdered sample containing phenobarbitone (**I**) (≃ 2·5 mg) and acetylsalicylic acid (**II**) (≃ 100 mg) in the buffer soln. and apply the slurry to a column of the prepared resin. Elute **I** by passing more buffer soln. (≃ 200 ml) during ≃ 3 hr.; adjust the pH of the eluate to about 11·2 by the addition of 5 *N* NaOH and measure the extinction at 250 mμ. Elute **II** with *M* aq. NH_3 (≃ 400 ml) for ≃ 4 hr. and measure the extinction at 297 mμ. Calculate by the use of standard curves. A. R. ROGERS

3482. **Size analysis of phenothiazine.** M. J. Thornton (I.C.I. Ltd., Pharm. Div., Alderley Park, Ches., England). *J. Pharm. Pharmacol.*, 1959, **11** (Suppl.), 127T–138T.—Results are given for the analysis of particle-size distribution of a sample of finely ground phenothiazine by (*a*) microscope counting, (*b*) the Andreason pipette (a fixed position

pipette method), (*c*) the Stairmand apparatus (a liquid column method with sediment extraction), and (*d*) the Micromerograph (a gas column method with sediment accumulation). Each method is reproducible, but the results differ considerably. The advantages and disadvantages of each are discussed briefly and a means of comparing the results with those obtained by surface-area measurements is given. A. R. ROGERS

3483. **Chromatographic detection of meprobamate.** J. L. Emmerson and T. S. Miya (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2104.—An earlier method (*cf.* Walkenstein *et al.*, *J. Pharmacol.*, 1958, **123**, 254) has been modified. The chromatogram is run and air-dried to remove the solvent, then placed in an atmosphere of Cl gas for 15 min., removed and sprayed immediately with aq. fluorescein sodium soln. When viewed under u.v. light the meprobamate spots appear dark against a fluorescent background. Spots of 3 to 5 μg can be clearly seen. G. P. COOK

3484. **The pharmacy of chlorothiazide (6-chloro-7-sulphamoylbenzo-1:2:4-thiadiazine 1:1-dioxide): a new orally effective diuretic agent.** W. F. Charnicki, F. A. Bacher, S. A. Freeman and D. H. DeCesare (Merck Sharp & Dohme Res. Lab., West Point, Pa.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (11), 656–659.—To determine chlorothiazide (**I**) in tablets or in the sodium salt, prepare a 0·001% soln. in 0·1 *N* NaOH and measure the extinction at 292 mμ within 1 hr. To determine **I** in the oral suspension, prepare a soln. in 0·1 *N* HCl, extract acidic and phenolic impurities with $CHCl_3$ and discard the extract, render the aq. phase alkaline and complete as described above. The main product of hydrolytic decomposition of **I** is not removed by this treatment and its absorption at 292 mμ is about 25% of that of **I**; it may be determined by diazotisation and coupling with N-1-naphthylethylenediamine. A. R. ROGERS

3485. **A colorimetric determination of azacyclonol.** Kiichiro Kakemi, Toyozo Uno and Hajime Yamashina (Pharm. Inst., Med. Fac., Kyoto Univ., Sakyo-ku). *J. Pharm. Soc. Japan*, 1959, **79** (4), 440–443.—The determination of azacyclonol (diphenylpiperid-4-ylmethanol hydrochloride), a tranquilliser, in aq. soln. and in urine was carried out colorimetrically. An aq. soln. (5 ml) of the sample, 0·3% aq. Na 1:2-naphthaquinone-4-sulphonate soln. (1 ml) and 10% Na_2CO_3 soln. (1 ml) are mixed and allowed to stand for 10 min. at room temp. The mixture is cooled with ice and extracted with $CHCl_3$ (4 ml). After drying the $CHCl_3$ soln. over Na_2SO_4, the extinction is measured at 458 mμ. For a urine sample, the urine (10 ml) is treated with $(NH_4)_2SO_4$ (4 g) and 10% NaOH soln. (8 ml) and extracted with $CHCl_3$. The $CHCl_3$ layer is washed with Clark - Lubs buffer (pH 9·0), extracted with 0·1 *N* HCl (5 ml) and treated as for an aq. soln., and the coloured soln. is extracted with CCl_4. The extinction of the CCl_4 soln. is measured at 428 mμ. This method is used for the determination of the amount of the drug excreted after administration. S. NATORI

3486. **Applications of titration in non-aqueous solution. III. Determination of isoniazid and sulphafurazole in mixtures.** Satoshi Mizukami and Eizo Hirai (Res. Lab., Shionogi & Co., Ltd., Imafuku, Amagasaki, Hyogo-ken). *J. Pharm. Soc. Japan*, 1959, **79** (4), 454–457.—The separate determination of isoniazid (**I**) and sulphafurazole (**II**) by non-aq. titration was attempted by making use of the difference in the basicity and the solubility of their acetates. Treatment of the mixture of **I** and **II** with acetic anhydride and acetic acid at room temp. for 30 min. yields acetates of **I** and **II**; the latter is deposited from the soln., while the former remains in soln. **I** acetate in the soln. is titrated as a base with 0·1 *N* $HClO_4$, while **II** acetate is separated, dried, dissolved in ethanol and titrated as an acid with 0·1 *N* Na methoxide.

IV. Determination of salts of phenothiazine bases. Satoshi Mizukami and Eizo Hirai. *Ibid.*, 1959, **79** (4), 457–460.—The determination of organic salts and hydrochlorides of chlorpromazine, promethazine, diethazine and their preparations was examined by non-aq. titration. The use of neutral or almost neutral solvents, such as acetone and methyl cyanide, gave better results than acid solvents such as acetic acid. One mole of these salts was titrated as one equivalent with glacial acetic acid soln. of $HClO_4$ by the use of a mixed indicator of methyl violet and bromocresol green; promethazine methylenedisalicylate was titrated as two equivalents. Good results were obtained with powders of sparingly soluble organic acid salts by back-titration with acetic acid soln. of triethylamine. S. NATORI

3487. **Organic analysis. XVI. Ultra-violet spectral study of substituent effect on benzenesulphonamide.** Tsutomu Momose, Yo Ueda and Shujiro Goya (Pharm. Inst., Med. Fac., Univ. of Kyushu, Fukuoka). *Chem. & Pharm. Bull., Japan*, 1959, **7** (8), 858–861 (in English).—The absorption spectra of benzenesulphonamide and 46 of its *p*- and N-substituted derivatives have been measured in 95% ethanol, and data are reported.

XVII. Ultra-violet spectra of phenyl sulphone derivatives. Tsutomu Momose, Yo Ueda and Shujiro Goya. *Ibid.*, 1959, **7** (8), 862–863 (in English).—The absorption spectra in 95% ethanol of 25 of the *p*- and ω- substituted derivatives of methyl phenyl sulphone have been measured, and data are reported. A. R. ROGERS

3488. **Activation analysis of certain arsenic- and antimony-containing pharmaceuticals and the effect of beta-emitting isotopes.** D. G. Kaiser and J. E. Christian (Sch. Pharm., Purdue Univ., Lafayette, Ind.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (11), 650–652.—To determine As in oxophenarsine hydrochloride (**I**), carbarsone (**II**) or As_2O_3 (**III**), or Sb in antimony potassium tartrate (**IV**) or stibophen (**V**), irradiate the sample (≃ 0·1 g) with slow neutrons at a flux of about 10^6 per sq. cm per sec. for 1 to 2 days, dissolve in water (for **I** and **V**), aq. NaOH (for **II** and **III**) or aqua regia (for **IV**), set aside for 1 to 2 days and use a γ-ray scintillation spectrometer to count the radiation at 0·558 MeV (for **I**, **II** and **III**) or 0·566 MeV (for **IV** and **V**). The average error is ≃ 5%. The effect of Bremsstrahlung resulting from microcurie amounts of ^{32}P produced during irradiation can be reduced by the use of 3-mm lead shields. Sample processing and chemical separations are not required. A. R. ROGERS

3489. **Thin-film chromatographic investigations of some organic nitrogen compounds used in pharmacy.** E. Nürnberg (Fa. E. Merck A.-G., Darmstadt). *Arch. Pharm., Berlin*, 1959, **292** (11), 610–620.—The thin-film chromatographic method of Stahl (*Pharmazie*, 1956, **11**, 633), involving the separation of mixtures on a silica gel - $CaSO_4$ film

dried on a glass plate, is discussed. Chromatograms prepared in this manner require only short development times and are resistant to strong mineral acids and similar spray reagents. Organic nitrogen bases may be separated by the addition of acids, bases or buffer soln. to the solvent system. The method is applied to the separation of mixtures of codeine, Ilvin (1-*p*-bromophenyl-3-dimethylamino-1:2′-pyridylpropane) and N-methylephedrine, of Decentan (3-chloro-10-{3-[4-(2-hydroxyethyl)-1-piperazine]propyl}phenothiazine) and its decomposition product, and of amino acids in protein hydrolysates.

A. G. COOPER

See also Abstracts—**3291**, Iodine in drugs. **3294**, Arsenic in org. compounds. **3301**, Reaction of $CHCl_3$ with bases. **3306**, Alkoxypropanediols in fish-liver oils. **3348**, Reactions of chromones. **3402**, Meprobamate in biological fluids. **3403**, Sulphanilamide in biological fluids. **3404**, Isoniazid in biological fluids. **3405**, 2:3-Dimethyl-1-phenyl-4-pyrrolidino-5-pyrazolone in biological fluids. **3406**, Psicofuranine in biological fluids. **3412**, Chromatography of deoxy sugars. **3414**, N-Glucuronides of sulphonamides. **3421**, Flavanones in drugs. **3508**, Saccharin and dulcin in mixtures. **3522**, Determination of vitamin A. **3539**, Determination of menaphthone.

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

3490. **Water determinations in white sugars according to the Karl Fischer titration method.** R. Hoffmann. *Zucker*, 1959, **12**, 274–278.—This method gives somewhat high values for water content, as compared with those by an oven-drying method. By standardising the reagent with a test sugar of exactly predetermined water content, this bias can be prevented, and results are then consistent with those obtained by the oven-drying method. The sugar must be analysed under the same conditions as the test sugar.

SUGAR IND. ABSTR.

3491. **Polarisation of standard sugar solutions at temperatures about 20° C.** E. Einsporn. *Zuckererzeugung*, 1959, **3**, 322–323.—The permissible changes in room temp. for sugar determination by polarisation are investigated. A table lists the corrections to be applied to the readings from 85° to 100° S at 14° ± 0·3° C to 26° ± 0·3° C on a saccharimeter standardised at 20° C. It is calculated that within this range the effect of materials expansion remains within the accuracy of reading the polarimeter, *i.e.*, 0·01° S. SUGAR IND. ABSTR.

3492. **Determination of the sucrose content in sugar beet by the isotope-dilution method.** H. Horning and H. Hirschmuller. *Z. Zuckerind.*, 1959, **9**, 499–507.—The isotope-dilution method with ^{14}C-labelled sucrose molecules has been investigated. The β-radiation is measured (impulses per min.) in a flow-counter filled with methane. From the ratio in specific activity between added and found sucrose, its content can be calculated. Radioactive sucrose is crystallised from alcoholic soln., dried with alcohol and acetone and stamped into tablets. This sucrose (1 g) is added to ≃ 15 g of rasped beet slurry, which is then cooled, freeze-dried and extracted with diethylamine. The sugar is crystallised and dissolved in a $CuSO_4$ soln., from which the sucrose - $CuSO_4$ complex precipitates. This complex is dissolved in water and filtered, and 2:4:6-trimethylpyridine is added to precipitate the $CuSO_4$. The filtrate is evaporated, and the sugar is crystallised, dried and pressed into 300-mg tablets. The statistical error in measuring the number of impulses is of about the same magnitude (0·06%) as in polarisation. Results obtained so far with this method with 12 beet samples stored for different times at low temp. show that in normal beet samples the sucrose content found is higher than that obtained by the usual methods; after storage for several weeks the sucrose content found is, on the contrary, lower than that found by other methods. This may be explained by the formation during storage of compounds having greater optical activity than sucrose. This possibility has also been indicated previously by paper-chromatographic analyses. Results obtained by this isotope method of analysis may lead to a revision of yield calculations, indicating that the storage losses are in effect larger than those assumed so far. SUGAR IND. ABSTR.

3493. **Rapid factory analyses for the determination of invert sugar, lactic acid and amino acids in sugar-factory products.** V. Prey, O. Szabolcs and I. Szabolcs. *Z. Zuckerind.*, 1959, **9**, 614–617.—Invert sugar in juices is determined by reaction with triphenyltetrazolium chloride (**I**) to give the formazan which is measured colorimetrically. The sample is first dried in a sintered-glass cell, and is washed with ether to remove formaldehyde. The product is then treated with **I** soln. and KOH soln., with steam blown through from below for 1 min. The product is washed and then extracted with dioxan for the colorimetric determination. Suitable apparatus is described. Lactic and amino acids are determined by passing the sample through a mixed-bed ion-exchange resin and then eluting with aq. NH_3. Lactic acid in the eluate is measured colorimetrically after reaction with $CuSO_4$ and ethanolic thymol soln., and the amino acids in the eluate are similarly determined after reaction with the "blue value reagent" [$Cu(NO_3)_2$ and Na acetate]. If the juice contains much SO_2 or galacturonic acid, correction factors for lactic acid or invert sugar contents must be established by measuring the colour produced by testing the ammoniacal eluate with **I**. SUGAR IND. ABSTR.

3494. **Rapid paper-chromatographic determination of raffinose in sugar-factory products.** V. Prey and E. Hammer. *Z. Zuckerind.*, 1959, **9**, 341–342.—The use of calcined and impregnated (preferably with citric acid buffer soln. of pH 7) glass-fibre paper for the determination of raffinose permitted more rapid separation; ethanol - acetone - water (2:2:1) was used as solvent. A quantitative colorimetric determination was made with 0·1% codeine soln. in conc. H_2SO_4 as spraying reagent, which gives a red - violet colour with oligosaccharides. The sensitivity was ≃ 5 μg of raffinose (< 10% in a sucrose mixture), with an accuracy of ± 10%.

SUGAR IND. ABSTR.

3495. **Paper-chromatographic determination of raffinose in molasses.** R. Weidenhagen and H. Schiweck. *Z. Zuckerind.*, 1959, **9**, 443–445.—Molasses is freed from the non-sugars by lead acetate treatment, followed by treatment with anion and cation exchangers. The resulting soln., which contains only sugars, is subjected to paper chromatography. The area of the raffinose spot is measured by means of a planimeter, and the

raffinose content is determined from a reference curve. Control tests indicate that the raffinose to sucrose ratio remains virtually unchanged during the pre-treatment. The results obtained by this method show great differences from those obtained by the Clerget - Herzfeld method.

SUGAR IND. ABSTR.

3496. **Paper-chromatographic determination of raffinose.** F. Schneider, A. Emmerich, C. Reichel and H. Rother. *Zucker-Beih.*, 1956–1959, **3**, 95–102.—The raffinose in molasses can be determined by visual comparison of the spots produced by ascending paper chromatography with those obtained with test soln. of known concn. The error is 0·1 to 0·2% (absolute). For higher accuracy the photometric analysis of the eluted spots is recommended. The spots are eluted with water by shaking for 10 min. in a conical flask. Calcium resorcinol-4:6-disulphonate is used as colour reagent. Graphs show the relations between the modulus of extinction and the wavelength of light, the concn. of H_2SO_4 and of reagent, and the temp. Amino acids, betaine and the dye of the chromatogram did not appreciably influence the results. Average results were 0·03 to 0·06% low for raffinose. A comparison of results obtained with visual and photometric methods shows that the former are generally about 0·3% low, which is attributed to the interference of molasses salts. Determinations by the Clerget - Herzfeld method show, on the other hand, great deviations in both directions.

SUGAR IND. ABSTR.

3497. **Determination of betaine.** O. Szabolcs and V. Prey. *Z. Zuckerind.*, 1959, **9**, 517–518.—A rapid method for determining the betaine content of sugar juices by means of a weakly acid cation-exchange resin (Amberlite IRC-50) is described. The adsorbed betaine is eluted with 0·1 *N* NaOH. The point of betaine break-through is determined by a spot test with bromothymol blue (dark-blue colour), and the amount of eluate is measured until an Alizarin yellow R (C.I. Mordant Yellow 1) indicator turns deep red in a spot test (NaOH break-through). A blank test must be made to correct the amount of alkali used; 1 ml of 0·1 *N* NaOH ≡ 0·045 g of betaine. The precision can be increased by use of a potentiometric and/or conductimetric method instead of indicators for determining the inflection points of the titration curve. The relative accuracy is ≃ 5%.

SUGAR IND. ABSTR.

3498. **Method for the determination of total amino acids and glutamic and aspartic acids in sugar-factory juices.** V. Prey, L. Maier and O. Szabolcs. *Z. Zuckerind.*, 1959, **9**, 408–410.—The amino acids in thin juice diluted with water (1:1) (100 g) are adsorbed on a strongly acid ion-exchange resin (Amberlite IR-120) and then eluted with aq. NH_3. The eluate is evaporated to two-thirds of its vol. until about neutral. The soln. is then passed through a weakly acid cation-exchange resin (Amberlite IRC-50), and the percolate contains the free amino acids. The resin columns are each 20 mm in diam. and 50 cm long; the percolation rate is 1 or 2 drops per sec., increasing to 5 or 6 drops per sec. The acids are titrated with 0·1 *N* NaOH, with 10 drops of bromothymol blue indicator (0·25% in 96% ethanol) to the change from yellow to green, by which the glutamic and aspartic acids are measured. After the addition of 30% formaldehyde soln. (20 ml), made alkaline to the same green colour of bromothymol blue (which turns the soln. yellow), the total amino-acid content may be obtained by further titration with NaOH until the indicator is blue; 1 ml of 0·1 *N* NaOH ≡ 0·0147 g of glutamic acid or 0·133 g of aspartic acid.

SUGAR IND. ABSTR.

3499. **The nitrogenous non-sugars. III. Determination of glutamine in sugar factory juices.** F. Schneider, E. Reinefeld and H. Forth. *Zucker-Beih.*, 1956–1959, **3**, 102–107.—A method for the direct determination of glutamine in beet juices is described in detail. The glutamine is separated from glutamic acid by paper chromatography, with a butanol - water - acetic acid solvent mixture. The glutamine is eluted, and hydrolysed to glutamic acid in one step by boiling with 5% HCl for 1 hr. The glutamic acid is then determined by paper electrophoresis after evaporation of the HCl. The results may be in error by up to 4·5%. No formation of pyrrolidonecarboxylic acid (**I**) from glutamic acid was observed. Raw, thin and thick juices treated in different ways in a semi-technical plant gave results indicating that the glutamine content is strongly dependent upon the manufacturing conditions. Greater glutamine degradation with more energetic treatment leads to alkali losses and a lower pH. The glutamic acid content does not vary greatly and little is removed during defecation; the decrease in glutamine accounts for the corresponding increase in **I**. The glutamine is probably transformed directly to **I**, since the equilibrium between glutamic acid and **I** shows a preponderance of the latter at all stages of the manufacture.

SUGAR IND. ABSTR.

3500. **Ion-exchange method for determining total acid contents in sugar beets and sugar-factory juices.** K. Bohn. *Zuckererzeugung*, 1959, **3**, 272–276.—The method of determining total acid contents in raw, thin and thick juice and molasses by means of a strongly acid ion-exchange resin is described. The liquors (diluted if necessary) are passed slowly through the resin and the total percolate (with washings) is titrated with NaOH. The error of the method is $< \pm 1\%$. Amino acids and CO_2 are not measured. Microbiological infection of the juice sample must be prevented; if necessary, sterilisation should be carried out. Factors which affect the normal values for total acid contents are discussed.

SUGAR IND. ABSTR.

3501. **Application of Baudouin test to the analysis of honey. A new test for the detection of "HMF."** S. N. Mitra, T. V. Mathew and A. K. Mallik (Central Food Lab., Calcutta). *J. Instn Chem., India*, 1959, **31** (4), 175–176.—The hydroxymethylfurfural (HMF) is extracted from the honey (5 g) with ether (3 × 10 ml). After treating the evaporated extract with 0·5 ml of ethanol followed by 3 ml of conc. HCl, the addition of 3 ml of pure, fresh sesame oil gives a brilliant red colour (after 30 sec.) in the presence of HMF.

P. M. KINGSTON

3502. **Determination of volatile components of foodstuffs. Techniques, and their application to studies of irradiated beef.** C. Merritt, jun., S. R. Bresnick, M. L. Bazinet, J. T. Walsh and P. Angelini (Pioneering Res. Div., U.S. Army Quartermaster Res. and Engng Cent., Natick, Mass.). *J. Agric. Food Chem.*, 1959, **7** (11), 784–787.—An account is given of methods and apparatus used for the distillation of volatile components from 200 to 500-g samples of foodstuffs. The sample is cooled to −196° at a pressure of 1 micron, and then allowed to warm to room temp.; volatile compounds

are received in a flask at −196°. The condensate consists mainly of water and CO_2, with less than 1% of odorous compounds; CO_2 is separated by warming the condensate to −140° and collecting the CO_2 at −196°. Other components can be separated from water at −80°. The CO_2 fraction from meat was submitted to gas chromatography, and the compounds were identified by mass spectrometry as methanethiol, dimethyl sulphide, methyl formate, acetaldehyde, acetone, methanol, ethanol and ethyl methyl ketone. The same fraction from irradiated meat contained larger amounts of these compounds, and also dimethyl disulphide and ethane- and *iso*-butane-thiols. M. D. ANDERSON

3503. **Determination of traces of cyanide in fish tissue.** K. Marsden (Freshwater Fisheries Lab., Pitlochry, Perthshire, Gt. Britain). *Analyst*, 1959, **84**, 746–747.—An aliquot of a homogenate with water of filaments excised from the gills is placed in the outer chamber of a Conway diffusion unit containing 0·1 *N* NaOH in the inner chamber. The homogenate is acidified with warm (30°) dil. H_2SO_4 and the unit is set aside for 3 hr. An aliquot of the liquid in the inner chamber is then removed, its pH is reduced to $\simeq 5$ by addition of acetic acid and it is diluted with H_2O. Chloramine-T soln. is added and then a pyridine - pyrazolone reagent (prep. described). After 30 min. the extinction of the suitably diluted liquid is measured against a reagent blank at 630 mμ and referred to a calibration graph. The mean recovery for additions up to 2 μg is 97·7% and the standard error is 1·11%. A. O. JONES

3504. **Neutral reagent for the routine determination of fat in separated milk and low-fat products.** F. J. Macdonald (United Dairies Res. Lab., Wood Lane, London). *Analyst*, 1959, **84**, 747–749.—The neutral reagent previously described (*Anal. Abstr.*, 1960, **7**, 263) is modified for the determination of fat in separated milk or in products having a low fat content by substituting the polyoxyethylene derivative of sorbitol monolaurate (Tween 21) for that of sorbitol trioleate (Tween 85). The preparation of the reagent is described. The apparatus used is that specified for determining fat by the Gerber process (B.S. 696: Part 1: 1955), but the skim-milk butyrometer is used instead of the standard butyrometer. Application of the method to the determination of fat in separated low-fat milk, in chocolate-flavoured milk, in buttermilk, in fat-free yoghourt and in cottage cheese is described. The accuracy is equal to that of the Gerber method. A. O. JONES

3505. **The determination of cyanide residues in apples.** M. Feuersenger (Max-von-Pettenkofer Inst., Abt. Lebensmittelchemie, Berlin-Dahlem). *Dtsch. LebensmittRdsch.*, 1959, **55** (11), 277–280.—Retention of cyanide varies with variety of apple, fumigant concn. and contact time. After fumigation with 0·5% (v/v) HCN for up to 1 hr. and airing of the fruit for not less than 48 hr., the retained cyanide is < 2 p.p.m. *Procedure*—To finely cut apples (50 g) add water (50 ml), silicone anti-foam agent (3 drops) and 5% trichloroacetic acid soln. (5 ml), heat to 100° for 30 min. in a stream of N and collect the distillate in 5% NaOH soln. (1 ml) and water (3 ml). Add 1% picric acid soln. (2 ml), dilute to 10 ml and heat at 100° for 3 min., set aside at room temp. for 1 hr. and finally incubate at 25° for 10 min. and compare the yellow colour produced with standards treated similarly. E. C. APLING

3506. **Flame-photometric determination of calcium, magnesium and potassium in canned tomatoes.** B. S. Luh and G. Niketic (Dept. Food Technol., Univ. California, Davis). *Food Res.*, 1959, **24**, 305–309.—Canned whole tomatoes (2 samples) and canned tomato juice contained 0·750, 0·798 and 1·293 g of ash, respectively. The dissolved ash was subjected to flame photometry and found to contain Ca 44·3, 39·3 and 4·0, Mg 9·9, 11·8 and 9·9, and K 238·4, 238·4 and 281·2 mg per 100 g, respectively. Calcium had evidently been added during canning. Calcium was determined similarly after diluting with 1% EDTA soln. and filtering; a standard curve was obtained from EDTA soln. containing Ca. Corresponding values for Ca in the two whole tomato samples were 32 and 28 mg per 100 g, respectively. NUTR. ABSTR. REV.

3507. **Characterisation of vanilla and other plant extracts by paper chromatography.** H. P. Burchfield and E. A. Prill (Boyce Thompson Inst., Yonkers 3, New York). *Contr. Boyce Thompson Inst.*, 1959, **20**, 251–263.—Extracts are diluted five-fold with ethanol and chromatographed on Whatman No. 1 paper in one dimension with a solvent containing KOH (20 g), NaBr (100 g) and ethanol (200 ml) made up to 1 litre with water, a solvent containing *iso*propyl alcohol (240 ml), conc. aq. NH_3 (150 ml), NaBr (84 g) and water (450 ml), and a solvent comprising acetic acid, HCl and water (30:3:10). Examination under u.v. light, after development of fluorescent pigments with 2% N-dodecyldimethylamine in $CHCl_3$, provides a method for identifying materials of botanical origin and, since intensity of fluorescence is proportional to concn., a measure of dilution can be detected. E. G. BRICKELL

3508. **Studies on the analysis of drugs by the use of the infra-red spectrum. I. Determination of saccharin and dulcin in a mixture by the potassium bromide pellet method.** Yūzo Nagase, Shigeo Baba and Michio Suzuki (Coll. of Pharm., Kashiwagi, Shinjuku-ky, Tokyo). *J. Pharm. Soc. Japan*, 1959, **79** (6), 705–708.—Separate determination of saccharin and dulcin (*p*-ethoxyphenylurea) in mixtures was examined by the KBr pellet method, with key bands at 970 and 820 cm^{-1}, respectively. The limit of detection of each component was about 50 μg and the coeff. of variation were within ± 1·62% for both components. S. NATORI

3509. **Identification of synthetic dyes employed for colouring foods.** H. Onrust (Keuringsdienst voor Waren, Rotterdam, The Netherlands). *Chem. Weekbl.*, 1959, **55** (46), 637–640.—Water-soluble dyes can be isolated from the foodstuffs by fixation on wool in acid medium, followed by elution of the dye with dilute aq. NH_3, or by extraction with an organic solvent, *e.g.*, quinoline. The second method is preferred since a number of dyes decompose when they are treated according to the first method. After extraction the dyes are identified by horizontal - circular paper chromatography. Oil-soluble dyes can be isolated by adsorption on activated aluminium oxide and subsequent elution with ethanol. The presence of dyes in the eluate is established by reaction with $SnCl_2$ in conc. HCl. These dyes can also be isolated by extraction of a soln. of the fat in light petroleum with dimethylformamide. Water is added to the coloured dimethylformamide soln. and this mixture is extracted with $CHCl_3$. Identification of the dyes in this soln.

is carried out by chromatography on paper that is impregnated with liquid paraffin. Methanol - acetic acid - water (16:1:3) serves as the mobile phase. M. J. MAURICE

3510. **Method for the determination of propyl gallate in lard.** B. A. J. Sedláček, A. Tichá and J. Hátle (Inst. Nutrition Res., Prague). *Prûmysl Potravin*, 1959, **10** (11), 594–597.—*Cerimetric procedure*—Dissolve the sample (25 g) in light petroleum (150 ml) and extract the propyl gallate with H_2O (5 × 20 ml) at 50°. Filter the aq. phase into a flask, add ferroin as indicator and titrate rapidly with 0·004 *N* $Ce(SO_4)_2$ till the blue colour persists for ≮ 10 sec. An accuracy of 5% was achieved. *Colorimetric procedure*—Extract the propyl gallate as described above and dilute the aq. phase to 100 ml. To 10 ml add ferrous tartrate soln. (0·1 g of $FeSO_4$ and 0·5 g of K Na tartrate in 100 ml) (1 ml) and dilute to 50 ml with Na acetate soln. (1%). Mix, set aside for 10 min. then measure the extinction at 510 mμ and compare with a calibration curve. The accuracy is ± 10%. The methods are claimed to be more accurate than that of Vos *et al.* (*Analyst*, 1957, **82**, 362). J. ZÝKA

3511. **Examination of coffee and coffee substitutes. V. Determination of soluble mannans in coffee infusions and extracts.** H. Thaler (Dtsch. Forsch.-Anstalt f. Lebensmittel-chemie, München, Germany). *Z. LebensmittUntersuch.*, 1959, **110** (6), 442–449.—A method is described for the estimation in coffee extracts of mannan. Dark-coloured products of roasting interfered with the Fehling method and the following procedure was developed. Coffee extract (5 g) is dissolved in boiling H_2O (30 ml), made up to 100 ml after cooling, and filtered twice. Aliquots (40 ml) are pipetted into each of two 100-ml centrifuge tubes, and 0·6 ml of glacial acetic acid and 2·5 ml of $NaClO_2$ soln. (40%) are added to each tube. The tubes are heated to 70° to 75°. After 30 min., 0·5 ml of glacial acetic acid and 2 ml of $NaClO_2$ soln. are added; this process is repeated after 60 min. and the tubes are left in the water bath for a further 90 min., after which they are cooled to room temp. in diffused daylight. Sodium bisulphite soln. (50%) (3 ml) and, after shaking, 15 ml of KOH soln. and 20 ml of mixed Fehling soln. are added. The tubes are kept overnight at 0° to 5°, after which they are centrifuged for 30 min. The supernatant liquid is poured off and 40 ml of KOH soln. (4%) is added and centrifuged again for 15 min.; this process is repeated twice more. The copper - mannan complex is dissolved in 1 ml of glacial acetic acid and any cuprous oxide which may have formed in spite of the cooling can be dissolved in one drop of H_2O_2 (100 vol.). Methanol (85 ml) is added, the mixture is stirred, left for 3 to 5 hr., stirred again and left overnight. The pptd. mannan is washed quant. into a weighed glass filter-crucible with a mixture of 100 ml of methanol and 5 ml of glacial acetic acid, dried to constant weight at 130°, then ashed at 800°. Mannan (%) = 100 × [(wt. of ppt. — wt. of ash) × 2·5/wt. of sample]. The accuracy is within ± 2·5%. The mannan content of coffee infusion was between 7·5 and 11% of the extractive matter, whilst that of caffeine-free coffee contained only 4·3 to 6·4%. Various coffee extracts contained 3·5 to 10·5% of mannan, with the exception of two samples which contained only 3·0% and 2·4%. I. DICKINSON

3512. **The analysis of spirits by vapour-phase chromatography.** A. Fouassin (Lab. de Bromatologie, Inst. de Pharm., Univ. de Liège, Belgium). *Rev. Ferment.*, 1959, **14** (5), 206–212.—The determination of alcohols, aldehydes and water in a variety of spirits using columns of Carbowax, triethanolamine and diglycerol, and hydrogen as the carrier gas, is described. J. V. RUSSO

3513. **The detection of butylated hydroxyanisole in fats.** J. Wurziger and U. Chandra (Chem. und Lebensmitteluntersuchungsanst., Hyg. Inst., Hamburg). *Dtsch. LebensmittRdsch.*, 1959, **55** (11), 281.—The colour reaction with 2:6-dichloro-*p*-benzoquinone-4-chlorimine is not specific for butylated hydroxyanisole (**I**), but the presence of **I** may be confirmed by means of its colour reaction with ethanolic KOH soln. Gallates, nordihydroguaiaretic acid (**II**) and butylated hydroxytoluene (**III**) also give red colours with ethanolic KOH soln., but the colour due to gallates rapidly changes to yellow - brown, that due to **II** changes to yellow - brown on heating, and that due to **III** is ether-soluble. For the detection of **I**, heat the fat (5 g) under reflux with 2 *N* ethanolic KOH (2 ml) for 2 hr., add water (10 ml), then cool. In the presence of > 0·004% of **I** a pink to red colour slowly develops, reaching a maximum after 12 hr. Smaller quantities may be detected by alkali treatment of an ethanolic extract of the fat. If the saponified soln. is dark brown, or for final confirmation, let stand for 12 hr. and pass the soln. through a 10-cm column of alumina. In the presence of **I** the percolate is pink or red. E. C. APLING

3514. **Determination of *cis*-unsaturation in oils by near-infra-red spectroscopy.** A. J. Fenton, jun., and R. O. Crisler (The Procter and Gamble Co., Cincinnati, Ohio). *J. Amer. Oil Chem. Soc.*, 1959, **36** (12), 620–623.—The difference between iodine value and infra-red *trans*-analysis indicates the degree of *cis*-unsaturation, but the direct method developed here is more rapid and less costly because only a single measurement is required. The Cary Model 14 spectrophotometer was used throughout this investigation. The *cis*-unsaturation present in refined oils, hydrogenated oils and finished shortenings was determined. Molar absorptivity measurements indicate that similar methods are applicable to the analyses of mixed esters or fatty acids. The method relies on the measurement of a band caused by *cis*-unsaturation in the near infra-red (2·143 μ). It was found that the areas under the absorption bands for *cis*-polyenes are integral multiples of the areas under the bands of *cis*-monoenes. The *cis*-content of oils which contain less than 10% of *trans*-triglycerides can be determined accurately by measuring the area under the absorption band of *trans*-fatty acids, if a point baseline is used and the peak absorption is measured. I. DICKINSON

3515. **Applications of infra-red spectrophotometry in the analysis of olive oil.** A. Arpino and G. S. Ricca (Staz. Sper. Olii e Grassi, Milan). *Olii Min.*, 1959, **36** (12), 493–498.—In contrast to the operations of degumming, de-acidification, decolorisation and deodorisation, esterification causes some elaidinisation of the unsaturated fatty acid groups, which is revealed spectroscopically by the absorption at 10·36 μ. Autoxidation of the oil also increases the absorption in this region, and that at 2·9 μ, owing to the presence of –OH and –OOH groups. L. A. O'NEILL

3516. **Quantitative estimation of the fatty acids of olive oil.** J. Gracián, E. Vioque and M. Pilar de la Maza (Inst. de la Grasa, Seville, Spain). *Nature*, 1959, **184** (Suppl. No. 25), 1941.—The unsaturated acids are determined by spectrophotometry (*cf.* "A.O.C.S. Tentative Method Cd7-48") and the saturated acids are separated according to Bertram (*Z. Untersuch. Lebensmitt.*, 1928, **55**, 179) and quantitatively determined by treatment with cupric acetate followed by dithio-oxamide (*cf.* Vioque *et al.*, *Anal. Abstr.*, 1959, **6**, 2781). Comparative analyses of olive oil by the distillation of the methyl esters, the determination of the thiocyanogen values, gas chromatography and the proposed combination of spectrophotometry and paper chromatography showed good agreement.

S. Baar

3517. **Simplified technique for analysis by alkali isomerisation.** H. B. White, jun., and F. W. Quackenbush (Dept. of Biochem., Purdue Univ., Lafayette, Ind.). *J. Amer. Oil Chem. Soc.*, 1959, **36** (12), 653–656.—A new technique, referred to as the "bottle method", is described in which the sample is isomerised with K *tert.*-butoxide in a reagent bottle at 60° for 20 hr. Linoleic acid and linolenic acid were determined in 5 seed oils and the results were compared with the KOH - ethanediol method ("Official and Tentative Methods of Analysis", A.O.C.S., Chicago, 1946 rev. to 1958). Absorption at 233 mμ and 268 mμ was measured with a Beckman DU spectrophotometer, and the absorptivity values were calculated. Good agreement was obtained for linoleic acid, but the "bottle method" gave slightly higher results for linolenic acid.

I. Dickinson

3518. **Method for the extraction of free fatty acids from lipid material.** L. R. Mattick and F. A. Lee (New York State Agric. Exp. Sta., Cornell Univ., Geneva, U.S.A.). *Food Res.*, 1959, **24**, 451–452.—The sample is dissolved in ether - light petroleum - 95% ethanol (14:14:5) and is then extracted successively with 1% Na_2CO_3 soln., a mixture of 95% ethanol and 1% Na_2CO_3 soln. (1:6) then (1:4), and finally with water. All four aq. extracts are combined, and acidified with 10% H_2SO_4. The fatty acids are extracted three times with ether - light petroleum (1:1).

Nutr. Abstr. Rev.

3519. **New colorimetric determination of higher fatty acids.** Yoji Iwayama (Pharm. Fac., Osaka Univ., Toyonaka, Osaka-fu). *J. Pharm. Soc. Japan*, 1959, **79** (4), 552–554.—Ayers' method for the determination of fatty acids (*Anal. Abstr.*, 1956, **3**, 3674) was improved as follows. A sample of fatty acid is dissolved in $CHCl_3$ to give a 0·0005 to 0·02 *M* soln., 10 ml of the soln. is shaken with 5 ml of copper - triethanolamine reagent [*M* triethanolamine - *N* acetic acid - 5% $Cu(NO_3)_2$ soln. (9:1:10)], and the extinction at 670 mμ of the blue $CHCl_3$ layer is measured. This method can be applied to the determination of free and conjugated fatty acids in fatty oils and non-ionic surface-active agents.

S. Natori

3520. **Chromatographic separation of fatty acids based on chlorophenacyl esters.** A. C. Kibrick and S. J. Skupp (Biochem. Sect., New York Veterans Admin. Hosp., New York, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2057–2060.—The fatty acids are separated as their esters with *p*-bromophenacyl chloride on a column of polyethylene and Celite. The column is eluted with ethanol, and the individual fatty acid esters are identified by m.p. and extinction measurements at 257 mμ.

K. A. Proctor

3521. **Gas-chromatographic separation of long-chain fatty acid methyl esters on poly(vinyl acetate).** I. Hornstein, L. E. Elliott and P. F. Crowe (Meat Lab., Eastern Utilization Res. and Development Div., U.S. Dept. of Agric., Beltsville, Md., U.S.A.). *Nature*, 1959, **184** (Suppl. No. 22), 1710–1711.—To separate the methyl esters of stearic, oleic, linoleic and linolenic acids, apply the sample (5 μl) to a column (8 ft. × 0·19 in.) packed with 15% poly-(vinyl acetate) of mol. wt. $\simeq$ 1500 (Vinylite AYAC) on Chromosorb (30 to 60-mesh) and maintained at 205°. Pass He at 83 ml per min. and use a katharometer as detector. Quant. estimation within $\pm$ 5% is possible. Decomposition of poly(vinyl acetate) at this temp. is slight (0·5 mg per hr. per g), and the only volatile product is acetic acid.

A. R. Rogers

3522. **Simplified procedure for the determination of vitamin A.** J. A. Napoli, B. Z. Senkowski and A. E. Motchane (Control Spectrophotometric and Phys. Chem. Lab., Hoffmann-La Roche Inc., Nutley, N.J.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (11), 611–617.—In this modification of the procedure of the U.S.P. XV, the products of saponification of the sample are extracted with a single 150-ml portion of diethyl ether, instead of with 4 smaller portions. The quant. recovery of vitamin A is complete, the time of analysis is greatly reduced, and the precision is increased by a factor of 2 or 3. There is no improvement in the reproducibility of the Morton - Stubbs correction factor.

A. R. Rogers

3523. **Estimation of vitamin C by agar diffusion.** A. H. Chaiet and L. Chaiet (Jonathan Dayton Reg. High School, Springfield, N.J., U.S.A.). *Nature*, 1959, **184** (Suppl. No. 19), 1487–1488.—Apply the aq. soln. of ascorbic acid ($\leqslant$ 1 mg per ml) to a 0·5-in. disc of S. & S. No. 740-E filter-paper and place the disc on 2% agar gel containing 0·08% of 2:6-dichlorophenolindophenol (**I**). Measure the diameter of the diffusion zone after 30 min. and calculate the concn. of ascorbic acid by the use of a standard curve. If 0·06% $KMnO_4$ soln. is used as indicator instead of **I**, the diffusion time can be extended up to 20 hr., but the results appear to be less reliable. With **I** as indicator, low results are obtained in the presence of $FeCl_3$ and some other iron salts. To eliminate the effect of acids other than ascorbic acid, the pH of the sample should be brought within the range 6·5 to 7·5 before assay.

A. R. Rogers

3524. **Spectrophotometric determination of α-tocopherol.** G. Lambertsen and O. R. Brækkan (Gov. Vitamin Lab., Norwegian Fisheries Res. Inst., P.O. Box 187, Bergen, Norway). *Analyst*, 1959, **84**, 706–711.—The soln. in light petroleum of the unsaponifiable fraction of the sample is applied to an alumina column. The chromatogram is developed with light petroleum and eluted with light petroleum containing 4% of diethyl ether. Equal fractions are collected and portions of each are tested for α-tocopherol with $FeCl_3$ and 2:2′-dipyridyl. Combined aliquots of the fractions containing tocopherol are evaporated and the residue is dissolved in acetone. The tocopherol is then separated by paper chromatography on duplicate

paper strips impregnated with squalane or liquid paraffin, with 85% aq. ethanol as ascending solvent. The tocopherol spots are located on one paper with $FeCl_3$ and 2:2′-dipyridyl, cut out from the duplicate strip, and extracted with ethanol, and the extinction of the extract is measured at 280, 292 and 301 mμ and compared with that of a standard amount of α-tocopherol. By continuing the elution of the column with light petroleum - ether, the fluorescent band of vitamin A may also be eluted and determined. A. O. JONES

3525. **Spectrofluorimetric determination of tocopherols.** D. E. Duggan (Nat. Heart Inst., Bethesda, Md., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **84** (1), 116–122.—Total and esterified tocopherols in tissues are determined by the fluorescence at 340 mμ of free tocopherols activated at 295 mμ. Plasma (2 ml) is diluted with ethanol and water and the total tocopherols are then extracted with hexane. Suitable internal standards are added to a further aliquot of the sample. After extraction and separation, a portion of the hexane is diluted with ethanol for determination of free tocopherols. The esterified tocopherols in another portion are hydrolysed with a $LiAlH_4$ reagent and the total determined similarly. Good agreement with results by chemical methods is attained. W. H. C. SHAW

3526. **Comparative vitamin B_{12} assay of foods of animal origin by *Lactobacillus leichmannii* and *Ochromonas malhamensis*.** H. Lichtenstein, A. Beloian and H. Reynolds (Human Nutrition Res. Div., Agric. Res. Service, U.S. Dept. of Agric., Beltsville, Md.). *J. Agric. Food Chem.*, 1959, **7** (11), 771–774.—Results are given for 27 products which were assayed in parallel. While the results for 15 of these were found to be generally of the same order of magnitude, the mean vitamin-B_{12} activity measured by *O. malhamensis* was significantly higher at the 5% level than that measured by *Lb. leichmannii*. It is thought possible that certain unidentified substances, other than vitamin B_{12}, in foods of animal origin stimulate the growth of *O. malhamensis*. In view of this it is suggested that both methods should be used for B_{12} assays. I. DICKINSON

See also Abstracts—**3306**, Alkoxypropanediols in fish-liver oils. **3447**, Paper chromatography of sterols in oils.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

3527. **Organic acids in a selected dialysate of air particulate matter.** E. D. Barber, F. T. Fox, J. P. Lodge and L. M. Marshall (U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio). *J. Chromatography*, 1959, **2** (6), 615–619 (in English).—A method for the resolution of mixtures of organic acids obtained from the particulate matter in air samples is described. A sample of particulate matter is shaken with 0·05 *N* NaOH for 5 hr. and then dialysed through Cellophane. The dialysate is evaporated to dryness, then re-dissolved in water, and the pH is adjusted to $\simeq 2$ with glycine buffer or HCl (1:1) or both. The soln. is added to a silica gel column and chromatographed, with the gradient elution technique. Unresolved mixtures of carboxylic acids in the eluate are converted into anilides with ^{14}C-labelled aniline and separated by paper chromatography, the positions of the anilide spots being detected by preparing radioautographs. G. S. ROBERTS

3528. **Spectrographic analysis of air samples for beryllium contamination.** M. P. Brash (Avco Corp., Wilmington, Mass.). *Appl. Spectroscopy*, 1960, **14** (2), 43–45.—A procedure for monitoring the beryllium content of air in establishments fabricating or machining beryllium is described. The sample is collected by aspirating a measured vol. of air through an analytical filter or cellulose acetate plastic filter, using either a permanently installed low-vol. sampler, consisting of a vacuum pump, flow-meter and a filter head or a commercially available portable high-vol. sampler. After wet-ashing, the sample is dissolved and analysed spectrographically by a rotating disc technique. Determinations down to 0·05 μg of Be per cu. ft. of air with a coeff. of variation of less than 11% are possible. The method has been applied with slight modification to the analysis of thoria, silica and silver air-borne toxic dusts. An extension of the procedure to include Pb and Hg is possible. G. P. MITCHELL

3529. **Further advances in the absorptiometric determination of dissolved oxygen.** J. Banks (C.E.G.B., Castle Donington Power Sta., nr. Derby, England). *Analyst*, 1959, **84**, 700–705.—In this method, simpler and more sensitive than that previously described (*Ibid.*, 1954, **79**, 170), the samples are taken by a specified procedure and the reagents are added to the bottles by means of hypodermic syringes through Suba-seal stoppers in the order alkaline KI soln., $MnSO_4$ soln., dil. H_2SO_4 and iodine soln. to the sample, and with the order of $MnSO_4$ soln. and dil. H_2SO_4 reversed to the blank. After mixing of the reagents, the stoppers are removed and a soln. of 3:3′-dimethylnaphthidine (**I**) in glacial acetic acid is added, and the extinction is measured against the blank in an absorptiometer with Ilford No. 605 filters. The calibration graph is prepared from dilutions of 0·001 *N* iodine to which $MnSO_4$ soln. and dil. H_2SO_4 and then the soln. of **I** have been added, the extinction being measured against the diluent soln. containing **I**. Ferrous iron must be removed from the sample and hydrazine must not be present. The precision is ± 0·0026 p.p.m. A. O. JONES

3530. **Determination of micro amounts of dissolved oxygen in water.** M. Needleman (Glasgow Univ. Mechanical Engng Res. Annexe, 49, Spencer St., Glasgow, Gt. Britain). *Analyst*, 1959, **84**, 720–725.—The determination of dissolved oxygen in the range 0·0 to 0·050 p.p.m. in an apparatus that allows the reagents used to be rendered oxygen-free is described. The apparatus is primarily intended for investigation of methods for determining dissolved oxygen, but with modification it could probably be used for the analysis of boiler water. The mean of the differences between the oxygen added and that found is nil, and the standard deviation of these differences is 0·0018 p.p.m. A. O. JONES

3531. **A rapid routine method for the micro-determination of dissolved oxygen in water.** J. Bargh (Marchwood Generating Station, C.E.G.B., Totton, Hants). *Chem. & Ind.*, 1959, (42), 1307–1311.—The sampling vessel consists of a bottle

(500 ± 5 ml in vol.) with an extended neck which forms a cup round a vacuum ground glass stopper; a stream of N is directed into the cup during reagent addition. Parallel samples are taken and one is used as a blank for determination of interfering substances in the sample or in the reagents. Ferrous iron must be absent. A correction for O in the reagents is made on a further pair of samples by adding double quantities of reagents to one and the usual amounts to the other. Standard Winkler reagents are used, and the KIO_3 and $Na_2S_2O_3$ titrations are performed by a "dead-stop" amperometric method. The sensitivity is ≃ 0·0004 ml of O per litre. P. D. PARR-RICHARD

3532. **Determination of the permanganate value for waters and sewage effluents containing nitrite.** P. V. R. Subrahmanyam, C. A. Sastry and C. S. Pillai (Dept. of Biochem., Indian Inst. of Science, Bangalore, India). *Analyst*, 1959, **84**, 731–735.—A comparison of the rates of destruction of nitrite by urea and sulphamic acid before the determination of the permanganate value of water, sewage effluents and sea water showed that sulphamic acid is the more effective reagent, the reaction being more rapid and a much smaller amount over the theoretical amount being needed. Unlike the reaction with urea, the reaction of nitrite with sulphamic acid is not retarded by H_3PO_4, a necessary acidifying agent for sea water and water containing much NaCl. A. O. JONES

3533. **Determination of cyanide in effluents.** F. R. Russell and N. T. Wilkinson (I.C.I. Ltd., Res. Dept., Alkali Div., Winnington, Northwich, Ches., England). *Analyst*, 1959, **84**, 751–754.—The filtered, diluted and slightly acidified sample is distilled with Zn acetate soln., the HCN being collected in three portions in separate stoppered cylinders containing 0·1 *N* NaOH. The temp. of the soln. in each cylinder is adjusted to 18° to 20°, the liquid is neutralised with 0·1 *N* HCl, one drop in excess being added. Bromine water is added and after 5 min. the excess of Br is removed with an arsenous acid soln. After another 5 min. a pyridine - benzidine hydrochloride reagent (prep. described) is added, the mixture is set aside in the dark for 20 min., and the extinction of each liquid is then measured in a Spekker absorptiometer with Ilford No. 604 filters. After correction for a reagent blank the absorption is referred to a calibration graph. Up to 3 p.p.m. of CN, present as CN^-, can be measured in the presence of up to 25 p.p.m. of CN, present as SCN^-, and up to 5 p.p.m. of CN, present as $Fe(CN)_6^{4-}$ or $Fe(CN)_6^{3-}$, in aq. soln. containing all these substances and also in the presence of NaCl and $CaCl_2$. A. O. JONES

3534. **Use of automatic analyser for continuous detection of sugar in evaporator condenser water.** E. H. Baum. *Tech. Pap. 18th Ann. Mtg Sugar Ind. Techn. Inc.*, Sect. IX, 1959. 5 pp.—Two instruments are used, one for determining the sugar in the river water used for condensers and the second for determining the sugar in water returned to the river. Each instrument consists of a proportionating pump, mixing coils, dialyser, heating bath, colorimeter and recorder. Sugar is inverted and reduces yellow $K_3Fe(CN)_6$ to colourless $K_4Fe(CN)_6$ in alkaline soln.; the extent to which the reduction has taken place is measured colorimetrically at 420 mμ in a continuous-flow cell. The addition of reagents to the samples is fully automatic. Replicas of the recordings obtained are given, together with a flow sheet. A working range of 0 to 400 p.p.m. of sugar was achieved.
SUGAR IND. ABSTR.

See also Abstracts—**3216**, Sulphates in waters. **3297**, Methane in mines. **3397**, Fluoride in waters.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

3535. **Rapid determination of exchangeable calcium and magnesium in highly leached soils.** P. B. H. Tinker (West African Inst. for Oil Palm Res., nr. Benin City, Nigeria). *Analyst*, 1959, **84**, 743–745.—The pH of the neutral soil extract in ammonium acetate soln. is adjusted to 12 to 12·5 in the presence of a NaOH - $Na_2B_4O_7$ buffer. Acid alizarin black SN (C.I. Mordant Black 25) indicator (prep. described) is added and the liquid is titrated for Ca until the colour changes from bluish pink to blue. For Ca plus Mg (plus Mn, if present) the extract is treated with KCN, and Eriochrome black T indicator is added. If the liquid is a clear blue, a magnesium soln. that has been titrated to the end-point of the indicator is added with aq. NH_3 and the liquid is titrated to a clear light blue or blue - green colour. A purple or red colour appearing when the indicator is added indicates the presence of Mn. Hydroxyammonium chloride is then added, the liquid is heated to ≃ 70°, the other reagents are added, and the liquid is titrated as before for the sum of Ca, Mg and Mn. Another portion of the extract is slightly acidified and the Mn is extracted with CCl_4 as its complex with diethyldithiocarbamate, and the aq. liquid is titrated as before for Ca plus Mg. If no clear end-point is obtained in any of these titrations, the presence of Fe is indicated. A little Na_2S is then added with the KCN before addition of the other reagents. A. O. JONES

3536. **Recent developments and current problems in inorganic analytical chemistry. Fertilisers.** K. D. Jacob (Soil and Water Conservation Res. Div., Dept. of Agric., Beltsville, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 1945–1949.—A review is presented of improvements in procedures and instrumentation, and of the use of new reagents and statistical appraisal of results, in the analysis of fertilisers. (76 references.) W. J. BAKER

3537. **Determination of free lysine ε-amino groups in cottonseed meals and preliminary studies on relation to protein quality.** B. P. Baliga, M. E. Bayliss and C. M. Lyman (Texas Agric. Exp. Sta., College Station, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **84** (1), 1–6.—The method is based on reaction of the ground sample with 1-fluoro-2:4-dinitrobenzene and $NaHCO_3$ at 40° for 22 hr. After removal of excess of reagent and hydrolysis with 6 *N* HCl the resulting dinitrophenyl amino acids are chromatographed on Whatman 3 MM paper developed with butanol - acetic acid - water (4:1:1). The band corresponding to ε-DNP-lysine is cut out, and eluted with *N* HCl, and the extinction measured at 363 mμ. Standards are prepared from ε-DNP-lysine hydrochloride (0 to 50 mg per 25 ml of HCl). Results were found to correlate with protein quality determined by rat-feeding tests. W. H. C. SHAW

3538. **Determination of inactivated procaine penicillin in premixes for feeding-stuffs and prepared feeds.** G. Machek and R. Brunner (Kontroll-Lab.

d. Biochem. G.m.b.H., Kundl, Tirol, Austria). *Sci. Pharm.*, 1959, **27** (3), 137–144.—The sum of procaine penicillin, procaine and *p*-aminobenzoic acid is determined colorimetrically by extraction followed by diazotisation and coupling with N-1-naphthylethylenediamine. A. R. ROGERS

3539. **Vitamin K_3 [menaphthone] and vitamin K_3 bisulphite [menaphthone sodium bisulphite]. Determination and comparison of stability in vitamin preparations for cattle feeding.** H. J. M. van Zijl and H. Geerling (Rijkslandbouwproefstation, Maastricht, Netherlands). *Chem. Weekbl.*, 1959, **55** (43), 597–602.—Menaphthone (**I**) is determined by coupling with 2:4-dinitrophenylhydrazine (**II**) and measurement of the blue colour produced on the addition of ethanolic NH_3 soln. (Novelli, *Science*, 1941, **93**, 358). Menaphthone sodium bisulphite (**III**) is determined by liberating **I** by hydrolysis with NaOH, extracting it with benzene, and determining it as before. *Procedure for* **I**—Heat the sample (10 g) to gentle boiling with benzene (50 ml) under reflux for 1·5 hr. Cool, and pass the clear supernatant liquid through a column of Floridin and wash the column with benzene (4 × 2 ml). Treat the combined percolate and washings with 1 ml of **II** soln. [0·25% in 12 *N* HCl - abs. ethanol (2:31)] and 1 ml of abs. ethanol, and heat for 1·5 hr. at 85° to 87° under reflux. Then add ethanol (5 ml) and evaporate to dryness under reduced pressure in an atmosphere of CO_2. Dissolve the residue in ethanol (5 ml) at 60°, cool and transfer the soln. to a 50-ml flask with ethanol (4 × 5 ml). Rinse the reaction flask with 5 ml of ammoniacal ethanol [20 ml of aq. NH_3 (sp. gr. 0·90) made up to 200 ml with 96% ethanol] by heating to 60°, cooling, and adding to the main soln. dropwise. Repeat this rinsing and addition three times. Make the combined soln. up to vol. with ethanol and read the extinction at 635 mμ against a blank prepared by treating 10 ml of benzene with 1 ml of **II** soln. and 1 ml of abs. ethanol and proceeding as described above. *Procedure for* **III**—Shake the sample (10 g) with water (100 ml) for 10 min. and, after the addition of 10 ml of 10% tannic acid soln., make up to 200 ml with water, then filter. Render an aliquot (50 ml) just alkaline to phenolphthalein with 0·5 *N* NaOH, and extract thrice with benzene (8 ml) and 96% ethanol (5 ml). Wash the combined benzene extracts with water (50 ml), add the washings to the aq. layer, re-extract this with benzene (8 ml) and add the benzene layer to the previous benzene extracts. Filter the benzene extracts into a 50-ml flask, make up to vol. with benzene that has been used to wash the separating-funnel and filter, treat a 10-ml aliquot with **II** soln. and abs. ethanol, and proceed as described above. It is found that **I** in feeding-stuffs decomposes rapidly, but that **III** is stable for several years. M. J. MAURICE

3540. **Analysis of substituted acetic acids used as herbicides. IV. Separation of trichloroacetic acid and 2:4-dichlorophenoxyacetic acid [2, 4 - D].** B. T. Milićević and S. Dj. Jankovic (Fac. of Civ. Engng, Lab. of San. Engng, Belgrade, Yugoslavia). *Bull. Soc. Chim. Belgrade*, 1958–9, **23–24** (1–2), 67–73.—Three procesures are given for separating trichloroacetic acid (**I**) and 2,4-D (**II**) by (*i*) ascending paper-strip chromatography, with H_2O as developer and bromophenol blue for spot detection, (*ii*) countercurrent distribution in a 25-tube Craig apparatus, and (*iii*) decomposition of **I** by reaction with NaOH. If **II** is present, the colorimetric determination of **I** by the Fujiwara reaction (*Sitzber. naturforsch. Ges. Rostock*, 1916, **6** 33) cannot be made.

V. Joint determination of 2:4-dichlorophenoxyacetic acid and 2:4:5-trichlorophenoxyacetic acid [2,4,5 - T] by the differential solubility method. B. T. Milićević and I. Lj. Kostic. *Ibid.*, 1958–1959, **23–24** (1–2), 75–77.—A mixture of the two acids is dissolved in acetone and the soln. is then titrated with H_2O to the first appearance of turbidity. The logarithmic curve for vol. (ml) of H_2O *vs.* concn. of acids is linear; the max. error is 2% and the method is considered suitable for soutine analyses. W. J. BAKER

3541. **Chromatographic analysis of technical 1-naphthylacetic acid.** L. Wiecheć and K. Hetnarska (Inst. Org. Ind., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (4), 747–753.—A method and apparatus for the analysis of technical products containing 1-naphthylacetic acid (**I**) in admixture with naphthylene-1:5-diacetic acid (**II**) are described. The chromatographic column is prepared with a mixture of 5 g of silica gel, 6 ml of buffer soln. (pH 6) and 30 ml of benzene satd. with the buffer soln. This is made into a 9-cm column by applying air under pressure; the liquid layer over the column should not exceed 2 mm. The dry sample (100 mg) is added and rinsed in with 2 ml of benzene. After drawing the soln. in, the prepared column is eluted with benzene under pressure at a rate of 2 ml per min.; 2-ml fractions are collected and titrated hot (after adding water and evaporating off the benzene) with 0·05 *N* NaOH to phenolphthalein. **I** was detected in fractions 7 to 17, which appears to be its usual position in the eluate; 2 or 3 further 2-ml fractions are titrated to ensure that elution is complete. When calculating the results a benzene blank is deducted. To determine **II** after removal of **I**, the column is eluted with diethyl ether satd. with buffer soln., and 8-ml fractions are titrated as described above. Eighteen 4-ml fractions are required to elute the **II**. The method was tested with standard mixtures; the relative error for **I** was 0·22% and for **II** 0·67%. L. SMAKOWSKI

3542. **Determination of organomercury residues in plant material.** M. G. Ashley (Plant Protection Ltd., Jealott's Hill Res. Sta., Bracknell, Berks., England). *Analyst*, 1959, **84**, 692–694.—Procedures for the determination of micro amounts of mercury in biological materials are reviewed. Techniques for the destruction of organic matter and the use of dithizone for the extraction stage and the avoidance of the simultaneous extraction of copper are discussed. Absorptiometric methods for determining the mercury - dithizone complex are described and also a photometric method in which the separated mercury is volatilised and its concn. in the vapour determined by means of a detector cell with a monochromatic light source, the output of a photocell being measured and referred to calibration measurements. No one method or combination of methods can be recommended without experimental results. (17 references.) A. O. JONES

See also Abstracts—**3216**, Sulphates in soil extracts. **3236**, Fluorine in mineral feeds. **3252**, Iron and manganese in soil and plants. **3289**, Fluorine in phosphoro- and phosphono-fluoridates. **3418**, Polarography of gibberellic acid. **3470**, Rotenone in plants.

5.—GENERAL TECHNIQUE AND APPARATUS

General

3543. **Graduated measuring cylinders.** British Standards Institution (2 Park St., London, W.1). B.S. 604 : 1952, Amendment No. 3 (8.3.60).—The amendment permits the longest lines to be continued to encircle the cylinder completely.

3544. **Some simple devices for micro-titration.** M. Pećar (Inst. of Inorg., Anal. and Phys. Chem., Univ. of Zagreb, Yugoslavia). *Microchem. J.*, 1959, **3** (4), 557–563.—A volumetric micro-burette, a gravimetric micro-burette and a titration table are described and illustrated. The burettes are of simple construction, with sealed-on reagent-reservoirs but no stopcocks. The titration table is of the key-press type and is fitted with springs which give sufficient vibration to provide adequate mixing of the sample soln. W. T. CARTER

3545. **Improvements in or relating to gas analysis [particularly the regeneration of spent caustic alkali from carbon dioxide gas-analysis apparatus].** H. Maihak A.-G. Brit. Pat. 831,039, date appl. 30.6.58; Germany, date appl. 29.6.57.—The exhausted alkali solution, *e.g.*, 25% KOH, is electrolysed, the CO_2 formed at the anode (platinum sheet formed on a core of synthetic resin) being prevented from mixing with regenerated alkali produced at the cathode (iron or nickel) by a diaphragm of aluminium oxide. The regenerated alkali is returned to the absorption chamber. The hydrogen resulting from the electrolysis is burnt to water and returned to the electrolytic vessel. J. M. JACOBS

3346. **The possibility of standardising gas regulation in gas-analytical metabolic studies.** S. Tannert (Med. Klinik, Med. Akad., Erfurt, Germany). *Z. anal. Chem.*, 1959, **170** (2), 408–412 (in German).—The construction of three simple gas-flow-control devices from glass capillaries and tubes packed with cotton wool is described. W. T. CARTER

3547. **Fractional micro-sublimation technique.** W. H. Melhuish (Inst. Nucl. Sci., D.S.I.R., Lower Hutt, N.Z.). *Nature*, 1959, **184** (Suppl. No. 25), 1933–1934.—A modification of the fractional sublimation technique described by Haussman (*Anal. Chem.*, 1954, **26**, 619) and Thomas *et al.* (*Ibid.*, 1958, **30**, 1954) is presented. A 15-mg sample is placed at the hot end of a glass tube (4 mm intern. diam.) kept at a temperature gradient by heating it electrically at one end. The components are eluted with N, which is passed at the rate of 10 ml per min., and move at different rates according to their vapour pressures. When applied to the purification of 9 : 10-diphenylanthracene this technique yielded at least 6 bands. Substances already purified by alumina chromatography could be further purified by this procedure. S. BAAR

3548. **Simple automatic vacuum regulation for the production of constant suction by water pumps at very variable water pressures.** S. Tannert (Med. Klinik, Med. Akad., Erfurt, Germany). *Z. anal. Chem.*, 1959, **171** (1), 1–4 (in German).—The apparatus is described and illustrated. B. B. BAUMINGER

3549. **Improved head and flask for miniature distillation.** A. G. Nerheim [Res. and Development Dept., Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1959, **31** (12), 2114.—The operation of miniature spinning-band distillation columns is improved by using the head and flask assembly described, which reduces leaks in the head and simplifies sample charging. K. A. PROCTOR

3550. **Remarks on extraction equilibria. II.** M. Oosting (Anal. Res. Inst. T.N.O., Rijswijk, Netherlands). *Anal. Chim. Acta*, 1959, **21** (5), 397–406.—The validity of the equations derived previously (*Anal. Chim. Acta*, 1959, **21**, 301) for the behaviour of metal ions during solvent extraction is confirmed for the extraction of Cu^{2+} and Ni^{2+} with 8-hydroxyquinoline and $CHCl_3$, respectively. The effects of pH and concn. of reagent are as predicted. W. J. BAKER

Chromatography, ion exchange, electrophoresis

3551. **Electrolytic chromatography.** A. Górski and J. Moszczyńska (Electrotech. Lab., Polish Acad. of Sci., Warsaw, Poland). *J. Chromatography*, 1959, **2** (6), 640–648 (in English).—A new method of chromatographic separation is described which is based on the deposition of metals from soln. of their salts on an electrode of variable potential. The separation of Ag, Zn, Cd and Cu into four distinct layers of metal from a soln. of the nitrates is reported. G. S. ROBERTS

3552. **Reduction chromatography of cations.** A. Górski and E. Kłoczko (Electrotech. Lab., Polish Acad. of Sci., Warsaw, Poland). *J. Chromatography*, 1959, **2** (6), 634–639 (in English).—Some success is reported in attempts to separate cations by passing them in neutral, ammonia or cyanide soln. through columns of powdered metal. The behaviour of the cations can to some extent be predicted from the differences in their standard potentials. G. S. ROBERTS

3553. **Variable solvent programmes for column chromatography.** R. P. Harpur (Inst. of Parasitology, McGill Univ., P.Q., Canada). *Anal. Chem.*, 1959, **31** (12), 2112–2113.—The apparatus described is a modification of that of Roberts and Mason (*Anal. Chem.*, 1956, **28**, 1063), and can be changed from one solvent programme to another in a few minutes. In the elution of a known mixture of organic acids the separations achieved were the same as those obtained by manual addition of the solvents. K. A. PROCTOR

3554. **Device to control channelling, voids and disruption of pressure-developed chromatographic columns.** W. G. Jennings (Univ. of California, Davis, U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2114.—The device described controls the formation of bubbles and voids within the column, and eliminates expansion and its effect on the column when the pressure is changed. K. A. PROCTOR

3555. **Spot distribution and size in paper chromatography.** J. C. Giddings and R. A. Keller (Dept. of Chem., Univ. of Utah, Salt Lake City, U.S.A.). *J. Chromatography*, 1959, **2** (6), 626–633 (in English).—A review that contains some original work by the authors is presented. Relationships between spot

area and spot content, and between spot length and spot content are given. Increase of spot area and spot length with time is also studied. (23 references.)
G. S. ROBERTS

3556. **The gas chromatograph as a semi-micro analyser for gases obtained from metals by vacuum extraction.** J. Václavínek (Státn. Výzkumný Úst. Mater. a Technol., Brno). *Hutn. Listy*, 1959, **14** (10), 905–909.—A mixture of H, N and CO is passed through a column containing activated charcoal. The carrier gas is CO_2. In a second column the CO is oxidised by a mixture of I_2O_5 and HIO_3 at 120° to 130°. The final gas-volume is determined in a nitrometer containing KOH soln., the difference in volume giving the amount of CO originally present. Gas pipettes are used for the transfer of samples; 0·5 ml of gas can be obtained by vacuum extraction from a metal. One determination takes 5 to 6 min. and the results show good reproducibility.
P. G.

3557. **Unexpected formation of volatile compounds on gas - liquid chromatography columns.** C. Weurman and J. H. Dhont (Central Inst. for Nutrition and Food Research T.N.O., Utrecht, The Netherlands). *Nature*, 1959, **184** (Suppl. No. 19), 1480–1481.—During the chromatography of methanol, ethanol and propanol on columns of 25% polyoxyethylene glycol 600 on HCl-washed firebrick (30 to 60 mesh), with N as carrier gas, peaks of the formates of the alcohols appear with anomalous retention times. It is thought that these esters are formed from breakdown products of the stationary phase and of the alcohols during the passage of the alcohols through the column.
A. R. ROGERS

3558. **Influence of column materials on gas-adsorption chromatography with silica gel.** K. Friedrich (Perkin-Elmer & Co. G.m.b.H., Überlingen, Bodensee, Germany). *J. Chromatography*, 1959, **2** (6), 664–666 (in German).—The tabulated retention volumes obtained from experiments with three different silica gels show that, of the C_1 to C_3 hydrocarbons, propane and acetylene is the only pair not effectively separated by all three materials, and that one silica gel (type Em, Firma Schuchart, Munich) separates all six components. A stability test of this material is reported.
E. G. CUMMINS

3559. **Use of coated tubing as columns for gas chromatography.** A. Zlatkis and H. R. Kaufman (Dept. Chem., Univ. Houston, Texas, U.S.A.). *Nature*, 1959, **184** (Suppl. No. 26), 2010.—In an investigation of the effect of sample load and diameter on efficiency, nylon tubing, 0·02 and 0·034 in. in diam., in 1000-ft. lengths, was coated with a 10% (w/v) soln. of substrate (squalane, hexadecane or *iso*quinoline) in dichloromethane or pentane, and samples were introduced with a syringe. The 0·02-in. tube was suitable for 1-mg loads, and the 0·034-in. column was successfully used with 2-mg sample loads. Efficiencies of up to 250,000 plates could be obtained on hydrocarbon samples of C_5 to C_7 paraffins and naphthenes. A nylon column 1 mile in length and with an inside diam. of 0·066 in. was coated in 1000-ft. lengths with hexadecane. This accepted samples up to 20 mg and gave efficiencies $> 10^6$ theoretical plates. From these results it was evident that sample loads for coated nylon columns are proportional to the available surface area or the amount of coating for the whole column.
S. BAAR

3560. **Evaluation of a commercial alkylarylsulphonate detergent as a column packing for gas chromatography.** D. H. Desty and C. L. A. Harbourn (The British Petroleum Co., Ltd., Sunbury-on-Thames, Middx., England). *Anal. Chem.*, 1959, **31** (12), 1965–1970.—Commercial household solid detergents, containing about 20% of alkylarylsulphonates, provide a useful general-purpose packing for gas chromatography. They are cheap, readily available and need little preparation before use, but the presence of inorganic salts renders them very hygroscopic so that columns not in use must be sealed from the atmosphere. The materials are moderately polar in character, stable at high temp., and are easily packed into long tubes. Their variable composition makes them unsuitable as a standard packing. The optimum temp. for max. resolution of a homologous series of normal paraffins is 75° to 85°.
K. A. PROCTOR

3561. **Sensitivity of katharometers in gas chromatography and the thermal conductivity of binary gas mixtures.** A. B. Littlewood (Dept. of Chem., King's College, Newcastle upon Tyne, England). *Nature*, 1959, **184** (Suppl. No. 21), 1631–1632.—The relative sensitivities of a katharometer to different vapours in dilute soln. in He are approx. directly proportional to their cross-sectional areas and are substantially independent of their thermal conductivities. The cross-sectional area of a molecule can be estimated by summation of contributions from the component structural units.
A. R. ROGERS

See also Abstracts—**3105**, Automation in chromatography. **3106**, Capillary analysis and paper chromatography. **3112**, Flavylium perchlorate as detecting agent.

Optical

3562. **Large-aperture grating spectrograph utilising commercial camera components.** A. M. Bass and K. G. Kessler (National Bureau of Standards, Washington, D.C., U.S.A.). *J. Opt. Soc. Amer.*, 1959, **49** (12), 1223–1225.—With the relatively inexpensive large-aperture lenses developed for standard photographic cameras, a spectrograph has been constructed in which the dispersing element is a plane replica reflection grating. Because of the glass lens components, the spectral range is limited to the visible and near-infra-red regions, 4000 to 11,300 A. The speed of the instrument makes it eminently suitable for the study of the spectra of relatively faint sources such as flames and glow discharges.
B. S. COOPER

3563. **Process for simultaneously sampling metals for spectrographic and chemical analysis.** W. R. Kennedy and R. N. Smith (American Cast Iron Pipe Co., Birmingham, Ala.). *Appl. Spectroscopy*, 1960, **14** (2), 53–54.—A new combination split mould is described, suitable for sampling ferrous metal for analysis. In one operation, the mould produces a composite cast sample, part chill-cast (suitable for spectrographic analysis) and part sand-cast (suitable for machining and subsequent chemical analysis). Variations in the basic mould design are given which produce special casting shapes, *e.g.*, pins and discs. The technique is also probably applicable to the sampling of non-ferrous metals.
G. P. MITCHELL

3564. **The use of amorphous carbon electrodes in high-voltage a.c. arc excitation.** J. Connor and S. T. Bass (Dept. of Agric. Chem., State Univ., East Lansing, Mich.). *Appl. Spectroscopy*, 1960, **14** (2), 55–56.—Controlled tests have been carried out, with combinations of graphite and amorphous carbon rods as counter and sample electrodes, in the spectrographic analysis of synthetic plant ash with high-voltage a.c. arc excitation. Results for the elements Ca, Mg, P, Fe, Mn and Cu showed a significantly higher precision when a carbon counter-electrode and a high arc current are employed ($\simeq$ 5 amp.); the precision is not affected by the use of either a carbon or a graphite buffer in the sample mix. Sensitivity of detection is favoured by a carbon - carbon combination, but it is concluded that the best possible choice is a carbon counter-electrode and a graphite sample-holding electrode.
G. P. MITCHELL

3565. **Use of thin-walled carbon electrodes [for spectrographic analysis].** O. N. Nikitina (Inst. of Silicate Chem., Acad. Sci. USSR). *Zavod. Lab.*, 1959, **25** (12), 1461–1463.—To increase the sensitivity of the determination of low contents of certain elements, the intensity of the CN bands is reduced by the use of thin-walled electrodes. Special cutters to give channels in carbon electrodes of depth 4 mm and diameter 2·5 mm, with a wall thickness of 0·25 mm, are described.
G. S. SMITH

3566. **Use of a plasma generator as excitation source in spectrographic analysis.** V. V. Korolev and É. E. Vainshtein (V. I. Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. of Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (6), 658–662.—A plasma generator is described. A stream of N is passed into the electrode space, a spark is struck, and, after the arc has been established, the spark discharge is switched off and the electrode gap increased as desired. A d.c. or impulse discharge is used. The plasma is ejected through a central channel in the cathode and appears as a flame more than 90 mm long. Its temp. depends on the diameter of the channel, the current strength and the intensity of cooling of the plasma by the N, and may be $>$ 10,000° K. The intensity of the lines from powders depends on the electrode gap. With a small gap the line intensity rapidly reaches a sharp maximum, and there is little fractionation of elements. As the gap is increased, fractional distillation of the elements begins to take place. The line intensity depends on the portion of the plasma flame which is spectrographed. The stability of this intensity is greater than in normal arc spectrography. Soln. are introduced into the source by atomisation into the stream of N, and show a much improved stability of line intensity. It is considered that the sensitivity obtained with the plasma generator is slightly less than with a d.c. arc, but the low background and the possibility of working without an optical system for illuminating the slit should enable the sensitivity to be increased. The high temp. is useful for determining elements which are otherwise excited only with difficulty.
C. D. KOPKIN

3567. **Influence of third elements in the spark spectrographic analysis of solutions.** A. K. Rusanov and L. I. Sosnovskaya (State Sci., Res. and Design Inst. of the Rare Metal Ind., Moscow). *Zhur. Anal. Khim.*, 1959, **14** (6), 643–657.—The thickness of the films formed on a rotating disc electrode is discussed in terms of the rate of rotation of the disc and the temp., viscosity and strength of the soln. Graphs are given for carbon and copper discs.
C. D. KOPKIN

3568. **Spectral analysis by the powder-sifting method. I. Technique.** J. Czakow (Polish Acad. Sci., Warsaw). Inst. Nucl. Res., Warsaw, Rep. No. 102/VIII, Aug., 1959. 22 pp.—A simple powder-sifting technique, in which a tripartite sifter electrode is employed, was developed for spectrographic analyses in a continuous or interrupted arc. The sensitivity of the method is higher than in the method of evaporation from cavities, and the precision is very high. The samples were excited from slightly modified conventional generators. The factors affecting sifting, including electrode temp., size and distribution of holes in the sifter electrode, type of electrical discharges, excitation atmosphere and sample characteristics are discussed.
NUCL. SCI. ABSTR.

3569. **Modified absorption cell and cell-compartment cover for the Beckman Model DU spectrophotometer.** S. R. Henderson and L. J. Snyder (Res. and Development Dept., Ethyl Corp., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2113.—The cell described has been designed to reduce the number of manipulations involved in colorimetric dithizone methods. In it the colour development, extraction and photometric measurement can all be performed rapidly and accurately, and it has been used for all types of colorimetric reactions. The cell as described can easily be modified to fit other spectrophotometers.
K. A. PROCTOR

3570. **Double-crystal X-ray monochromator-collimator.** R. S. Williamson and I. Fankuchen (Polytechnic Inst., Brooklyn, New York). *Rev. Sci. Instrum.*, 1959, **30** (10), 908–910.—A collimated monochromatic X-ray beam is obtained by successive reflections from two germanium or calcite crystals, arranged to have planes of incidence at right angles to one another.
G. SKIRROW

3571. **A theory of spectral excitation in flames as a function of sample flow.** M. R. Baker and B. L. Vallee (Biophysics Res. Lab., Harvard Med. Sch., Boston, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2036–2039.—From a study of cyanogen - oxygen and hydrogen - oxygen flames a theory has been evolved that is used to predict the inter-relationships between the flow rate of the aq. sample, flame temp., and the intensity of the spectral lines.
K. A. PROCTOR

3572. **Sample flow rate. A critical parameter of spectral excitation in cyanogen - and hydrogen - oxygen flames.** Keiichiro Fuwa, R. E. Thiers, B. L. Vallee and M. R. Baker (Biophysics Res. Lab., Harvard Med. Sch., Boston, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2039–2043.—The effects of flow rates of aq. soln. on the intensity of various spectral lines have been investigated and it was found that the optimum flow rate decreases with increase in flame temp. and excitation potential of the line measured.
K. A. PROCTOR

3573. **Factors affecting emission intensities in flame photometry.** W. H. Foster, jun., and D. N. Hume (M.I.T., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2028–2032.—The effects of various solution properties (surface tension, salt

concn., solution temp. and viscosity) that could affect the rate of addition of solution to the flame, the type of sample spray produced, or the composition or temp. of the flame have been studied. The total-consumption atomiser-burner system is compared with the reflux-type atomiser.

K. A. PROCTOR

3574. **Mutual cation interference effects in flame photometry.** W. H. Foster, jun., and D. N. Hume (M.I.T., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2033–2036.—Mutual cation interference effects with the alkali and alkaline-earth metals have been investigated with various flames and atomiser-burner systems. It has been established that these effects are true spectroscopic interferences, causing enhancement of the monochromatic radiation above continuous background. Several recommendations are made with regard to the optimum conditions for flame-spectrochemical analyses.

K. A. PROCTOR

3575. **Optical rotatory dispersion. I. A recording spectropolarimeter based on the Cary 11MS-50 spectrophotometer.** F. Woldbye (Tech. Univ., Copenhagen, Denmark). *Acta Chem. Scand.*, 1959, **13** (10), 2137–2139.—An accessory for the Cary 11MS-50 spectrophotometer has been developed that permits the automatic recording of optical rotatory dispersion in the wavelength range 806 to 228 mμ with a relative accuracy of $\simeq 1\%$.

N. E.

3576. **Universal apparatus for the rapid analysis of cement.** M. Wallraf (Forschungsinst. d. Zementind., Düsseldorf, Germany). *Z. anal. Chem.*, 1959, **170** (2), 420–423.—The apparatus comprises a combined colorimeter and turbidimeter. Its construction is briefly described and an outline is given of its use in the colorimetric determination of Al, Fe and Ti, the turbidimetric determination of SO_4^{2-}, and the EDTA titration of Ca and Mg.

W. T. CARTER

3577. **Optical system for measuring refractive indices.** Perkin-Elmer Corp. Brit. Pat. 830,930, date appl. 25.4.56; U.S.A., date appl. 28.4.55.—In an optical system, based on the Toepler Schlieren phenomenon, for determining the spatial variation of the refractive index of a substance, a beam of radiation passing through the substance contained in a Tiselius cell, and deflected according to the measure of the gradient of the refractive index, is incident upon an optical element having an optical separating line which is inclined with respect to the direction of the gradient of the refractive index. A trace corresponding to the course of the gradient of the refractive index is then produced by means of an astigmatic lens system, so designed that a second beam is passed through a standard medium, and the two beams of radiation form simultaneously a field of interference fringes that is distorted as a function of the course of the refractive index itself. The optical element is designed as a translucent phase-splitting device, the inclined separating line of which is determined by a sudden change in its optical thickness, so that in the plane of observation the trace is superimposed upon the field of interference fringes.

J. M. JACOBS

3578. **Use of the AZP (automatic Carl Zeiss 0·05 S [sensitivity] saccharimeter) in the sugar industry.** I. Becker. *Zucker*, 1959, **12**, 356–357.—The Zeiss saccharimeter is described and the results obtained in practice are discussed. By the use of a tube in which soln. are circulated, instead of the usual polarimeter tube, continuous analyses are possible. The results obtained can be recorded automatically if desired. The degree of accuracy is ± 0·05° S. Slightly turbid and/or coloured soln. can also be analysed with relative accuracy.

SUGAR IND. ABSTR.

See also Abstract—**3105**, Automation in spectrometry.

Thermal

3579. **General purpose thermometers.** British Standards Institution (2 Park St., London, W.1). B.S. 1704 : 1951, Amendment No. 2 (28.3.60).—Amendments relate to the finish of the top of stem and to inscriptions.

3580. **Secondary reference thermometers (Centigrade scale).** British Standards Institution (2 Park St., London, W.1). B.S. 1900 : 1952, Amendment No. 4 (28.3.60).—The amendment relates to inscriptions.

3581. **The electronic thermobalance and its application in the iron and steel works laboratory.** R. Strubl. *Stahl u. Eisen, Düsseldorf*, 1959, **79**, 298–303.—The work of the Czechoslovak Academy of Science on the development of an automatic electronic thermobalance for use in iron and steel works laboratories is reviewed and the equipment, including a furnace and a gas-analysis apparatus, is described. Several examples of application are given. (79 references.)

J. IRON ST. INST. ABSTR.

3582. **Apparatus for combined thermal analysis and dilatometry.** J. H. Pearce and P. G. Mardon (Metallurgy Div., A.E.R.E., Harwell, Berks., England). *J. Sci. Instrum.*, 1959, **36** (11), 457–460.—A system is described for carrying out automatically controlled and recorded simultaneous differential thermal analysis and dilatometry on small metallic samples at temperatures up to 1200° in a vacuum. A linear heating rate of the furnace is obtained by adjusting the output of a variable transformer by a motor-driven cam. The differential thermal analysis trace is obtained by amplifying the difference between a thermocouple embedded in the specimen and one mounted in an adjacent reference block (tantalum). G. SKIRROW

Electrical

3583. **Automatic determination of moisture in a gas by means of Fischer's reagent.** A. N. Korol', N. B. Znamenskaya and L. P. Losev. *Zavod. Lab.*, 1959, **25** (11), 1305–1307.—Automatic apparatus based on the use of Fischer's reagent and a dead-stop end-point titration is described.

G. S. SMITH

3584. **Amperometric titration with two indicator electrodes and allied techniques.** J. T. Stock (Dept. of Chem., Univ. of Connecticut, Storrs, U.S.A.). *Microchem. J.*, 1959, **3** (4), 543–555.—Recent developments in technique, and inorganic and organic applications are reviewed. (90 references.)

W. T. CARTER

3585. **Coulometric - acidimetric titrations in anhydrous media.** W. B. Mather, jun., and F. C.

Anson (State Inst. Technol., Pasadena, Calif., U.S.A.). *Anal. Chim. Acta*, 1959, **21** (5), 468–473.—Accurate titrations of potassium hydrogen phthalate and sodium acetate (in concn. $> 3 \times 10^{-4}$ milli-equiv.) can be made by the coulometric generation of H^+ in $\simeq$ 75 ml of a mixture of acetic anhydride and acetic acid (6:1, by vol.), with 0·1 *M* $NaClO_4$ as supporting electrolyte. Generation of H^+ proceeds with 100% efficiency by the anodic oxidation of a mercury electrode, and the titration can be followed potentiometrically with a glass electrode and a mercury - mercurous acetate reference electrode. Impurities in the $NaClO_4$ are corrected for by pre-titrating the supporting electrolyte to a potential inflection, adding an aliquot of the base, and then titrating to a second potential inflection; a small pre-determined correction for impurity in the acetic acid is also made. The method is applicable to the titration of μg amounts of bases (except easily acylated amines) that are too weak for titration in aq. acetic acid. W. J. BAKER

3586. **Parallel potentiometric titrations.** V. Pavelka and R. Palouš (Charles' Univ., Prague, Czechoslovakia). *Chem. Tech., Berlin*, 1959, **11** (11), 596–597.—The use of $AgMnO_4$ in potentiometry permits the simultaneous performance of argentimetric and manganimetric determinations. The normal potentiometric titration apparatus, with a S.C.E. as reference electrode, is used with two indicator electrodes (silver and platinum, respectively), each with its own circuit, so that the potential at either can be read at any time. A mixture of Na oxalate and KCl can be analysed to within $\pm$ 0·25% for each component.
J. P. STERN

3587. **Analytical applications of alternating-current cyclic voltammetry.** A. L. Juliard (Houdry Process Corp., Linwood, Pa., U.S.A.). *J. Electroanal. Chem.*, 1959, **1** (2), 101–107.—Peaks obtained are attributed to a change in nature of the surface of the electrode rather than to a change in the rate of diffusion through the soln. The reproducible differences obtained by the various methods of preparation of the platinum electrodes used are discussed. The negative-to-positive half-cycle can be used to estimate free iodine in a soln. containing $NaClO_4$ and KI. Calibration curves for KI, quinol, triethylamine and Na oxalate, all of which are oxidisable at potentials ranging from + 0·3 to + 0·9 V *vs.* the S.C.E., are reported.
E. G. CUMMINS

3588. **Determination of γ-ray abundance directly from the total absorption peak.** D. F. Covell (U.S. Naval Radiological Defense Lab., San Francisco, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1785–1790.—In the technique described, which is applicable to the determination of radionuclide abundances, the γ-ray activity is determined by using data obtained from scintillation spectrometer pulse-height distributions. The precision attainable is predictable, and the most favourable experimental conditions can be determined for each particular problem. The usefulness of the method can be extended by combining it with simple chemical procedures when these result in more favourable conditions for interpretation.
K. A. PROCTOR

3589. **Nuclear magnetic resonance in solids.** E. R. Andrew (Univ. Coll. of N. Wales, Bangor, Caernarvonshire). *Brit. J. Appl. Phys.*, 1959, **10** (10), 431–437.—A review, with a bibliography and 44 references, is presented. An account is given of the various interactions which generate the resonance spectrum and of associated spin-lattice relaxation mechanisms. E. G. CUMMINS

3590. **Activation analysis using neutrons from a radium - beryllium source.** G. Guében and J. Govaerts Monograph No. 2. Inst. Interuniv. des Sci. Nucléaire, Brussels. 1957. 131 pp.—The techniques and applicability of neutron activation analysis with a radium - beryllium source are discussed, and experimental results are given. Examples of practical application given are the determinations of Cu, V, Mn, Dy, Au, As, I, Ag, Cr and W. NUCL. SCI. ABSTR.

3591. **Simplified mass spectra with the aid of a field-emission ion-source.** H. D. Beckey (Inst. f. Phys. Chem., Univ., Bonn). *Z. anal. Chem.*, 1959, **170** (1), 359–364.—A potential of 20 kV applied to a fine point produces a field which ionises the gas sample without causing fragmentation. The spectra are therefore much simpler. Disadvantages lie in a lack of stability, sensitivity to interferences and the short life of the point electrode. G. BURGER

3592. **Continuous procedure for the mass-spectrographic determination of substances separated by gas chromatography.** D. Henneberg (Max Planck Inst. f. Kohlenforsch., Müllheim/Ruhr). *Z. anal. Chem.*, 1959, **170** (1), 365–366.—The gas issuing from a chromatograph passes directly into a mass spectrometer set at a definite mass number for each class of compound, chosen to give a strong peak with that class. The ratio of the heights of corresponding peaks on the mass spectrum and chromatogram is characteristic for each compound.
G. BURGER

3593. **High-molecular-weight mass spectrometry. Experience with a modified Metropolitan - Vickers MS 2 mass spectrometer.** E. Thornton and A. R. West (British Petroleum Co. Ltd., Sunbury-on-Thames, Middx., England). *Z. anal. Chem.*, 1959, **170** (1), 348–358 (in English).—The modifications permit the examination of materials with mol. wt. up to 800 with a resolution of 1 in 600 at a mass of 600. The modifications consist of the provision of a high-resolution source, an ion collector with variable slit width, a larger magnet, a galvanometer-type recorder and a heated glass inlet-system. Each of these, and the procedure for adjustment, are described in detail. The instrument has proved suitable for the analysis of lubricating oils and paraffin waxes. G. BURGER

3594. **New method of mass-spectrometric analysis of gas mixtures containing molecules of identical mass number.** I. Cornides (Dept. of Heavy Chem. Ind., Min. of Heavy Ind., Budapest, Hungary). *Z. anal. Chem.*, 1959, **171** (6), 431–433 (in English).—Certain gas mixtures (*e.g.*, CO and N) are difficult to analyse owing to the similar mass spectra of the components and the small fragment peaks as compared with the parent peak. The method described enables such mixtures to be analysed rapidly and with an accuracy of $\simeq \pm$ 1%. The spectrum is scanned at a fixed mass number (*e.g.*, 28) with varying electron energies. From the peak heights thus obtained (*e.g.*, at 70 and 30 *e*V), the partial pressures of the components can be calculated by means of values for the peak heights of the pure components at unit pressure. H. M.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
Colour Index	C.I.
concentrated	conc.
concentration	concn.
constant	const.
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_F
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{3+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions

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